

START

0034559

WHC-SD-EN-ES-043
Rev. 0

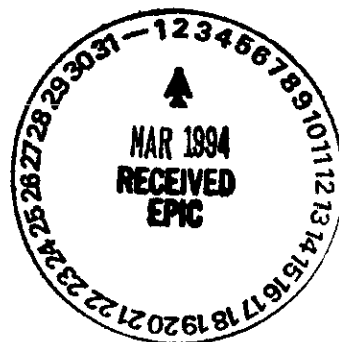
100 Area Groundwater Biodenitrification Bench-Scale Treatability Study -- Final Report

Prepared for the U.S. Department of Energy



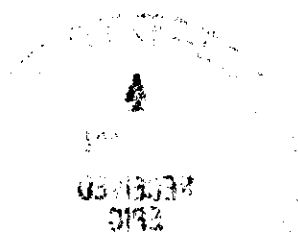
Westinghouse
Hanford Company Richland, Washington

Hanford Operations and Engineering Contractor for the
U.S. Department of Energy under Contract DE-AC06-87RL10930



Approved for Public Release

**THIS PAGE INTENTIONALLY
LEFT BLANK**



SUPPORTING DOCUMENT

1. Total Pages 112

<p>2. Title</p> <p>100 Area Groundwater Biodentrification Bench-Scale Treatability Study--Final Report</p>	<p>3. Number</p> <p>WHC-SD-EN-ES-043</p>	<p>4. Rev No.</p> <p>0</p>
<p>5. Key Words</p> <p>waste stream carbon data management dentrification remediation</p>	<p>6. Author</p> <p>Name: B.M. Peyton</p> <p>Signature: <i>Bunt M. Peyton</i> Feb 16, 1994</p> <p>Organization/Charge Code D7T34/P35A1</p>	
<p>7. Abstract</p> <p>Peyton, B.M., 1994, 100 Area Groundwater Biodentrification Bench-Scale Treatability Study--Final Report, WHC-SD-EN-ES-043, prepared by Pacific Northwest Laboratory for Westinghouse Hanford Company, Richland, Washington.</p>		
<p>8. PURPOSE AND USE OF DOCUMENT - This document was prepared for use within the U.S. Department of Energy and its contractors. It is to be used only to perform, direct, or integrate work under U.S. Department of Energy contracts. This document is not approved for public release until reviewed.</p> <p>PATENT STATUS - This document copy, since it is transmitted in advance of patent clearance, is made available in confidence solely for use in performance of work under contracts with the U.S. Department of Energy. This document is not to be published nor its contents otherwise disseminated or used for purposes other than specified above before patent approval for such release or use, has been secured, upon request, from the Patent Counsel, U.S. Department of Energy Field Office, Richland, WA.</p> <p>DISCLAIMER - This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.</p>		<p>10. RELEASE STAMP</p> <div data-bbox="1023 955 1477 1186"> <p>OFFICIAL RELEASE (11)</p> <p>BY WHC</p> <p>DATE FEB 22 1994</p> <p><i>Station # 12</i></p> </div>
<p>9. Impact Level 4</p>		

APPROVED FOR
PUBLIC RELEASE
1. Burkland
2/18/94

9407172846

**THIS PAGE INTENTIONALLY
LEFT BLANK**

SUMMARY

Biodenitrification is the biological conversion of nitrate and nitrite to gaseous nitrogen. This document describes the methodologies used and the results obtained in the bench-scale biodenitrification treatability tests at Pacific Northwest Laboratory. The tests showed that biodenitrification could reduce initial groundwater nitrate concentrations to less than 45 mg/L, the current maximum contaminant level (40 CFR 59569). Tests were carried out in anaerobic shake flasks to demonstrate nitrate removal and to determine the effects of carbon source and concentration, pH, and temperature on the denitrification ability of a Hanford denitrifying microbial consortia. Growth rates in the actual groundwater were slightly lower than in laboratory prepared simulated groundwater. The effects of pH and temperature are similar to what has been observed in other tests with different denitrifying microorganisms.

These tests were conducted under the guidance of Westinghouse Hanford Company, the 100-HR-3 Groundwater Treatability Test Plan (DOE/RL-92-73, Rev. 0), and the Treatability Study Program Plan (DOE/RL-92-48) using groundwater from 100-HR-3.

This report presents the test information in the format suggested by the Guide for Conductivity Treatability Studies Under CERCLA (EPA 1989) and includes additional denitrification process background information.

The results and conclusions contained herein were obtained specifically for the 100-HR-3 Groundwater Treatability Test. These results should not be construed or mistaken to be generally applicable to any other treatability study.

REFERENCES

40 CFR 59569, Part 248. December 24, 1974. U.S. Environmental Protection Agency. "Safe Drinking Water Act", Code of Federal Regulations.

U.S. Environmental Protection Agency (EPA). 1989. Guide for Conductivity Treatability Studies Under CERCLA, EPA/540/2-89/058.

9/13/22 9:08
0017016

CONTENTS

1.0	INTRODUCTION	1
1.1	SITE DESCRIPTION	2
1.1.1	Site Name and Location	2
1.1.2	History of Operations	2
1.1.3	Prior Removal and Remediation Activities	3
2.0	CONCLUSIONS AND RECOMMENDATIONS	3
2.1	CONCLUSIONS	3
2.2	RECOMMENDATIONS	6
3.0	TREATABILITY STUDY APPROACH	6
3.1	TEST OBJECTIVES AND RATIONALE	7
3.2	EXPERIMENTAL BACKGROUND	8
3.2.1	Experimental Principles	8
3.2.2	Carbon Limitations	9
3.2.3	pH Dependence	11
3.2.4	Temperature Dependence	12
3.2.5	Acetate and Methanol Comparison	13
3.2.6	Scale-up Issues	14
3.2.7	Phosphorous Requirements	15
3.2.8	Nitrite Production	15
3.2.9	Hanford Denitrifying Consortia	16
3.3	EXPERIMENTAL DESIGN AND PROCEDURES	17
3.4	EQUIPMENT AND MATERIALS	19
3.5	SAMPLING AND ANALYSIS	19
3.6	DATA MANAGEMENT	19
3.7	DEVIATIONS FROM THE WORK PLAN	20
4.0	RESULTS AND DISCUSSION	21
4.1	DATA ANALYSIS AND INTERPRETATION	21
4.1.1	Analysis of Waste Stream Characteristics	25
4.1.2	Analysis of Treatability Study Data	25
4.1.2.1	Presence of Inhibitory Compounds	25
4.1.2.2	Carbon Limitations	28
4.1.2.3	pH Dependence	36
4.1.2.4	Temperature Dependence	39
4.1.2.5	Acetate and Methanol Comparison	40
4.1.2.6	Large Volume Denitrification for Chemical Precipitation	41
4.1.2.7	Final Confirmation Testing	42
4.1.3	Comparison to Test Objectives	45
4.1.4	Recommended Bioreactor Designs	46

CONTENTS (cont)

4.2	QUALITY ASSURANCE/QUALITY CONTROL	48
4.2.1	Data Quality Objectives Definitions	48
4.2.2	Observed Data Quality	50
4.3	KEY CONTACTS	54
5.0	REFERENCES	54

APPENDIXES:

A	Raw Shake Flask Data	A-1
B	325 Laboratory Results	B-1
C	Suspended Solids Results and Observations	C-1
D	1993 Data Available from the HEIS Database for 100 Area 199-D5-15 and 100-H4-4	D-1

FIGURES:

3.1	pH effects on maximum denitrification rates	12
3.2	Schematic of custom made anaerobic flasks	19
4.1	Comparison of observed denitrification rates	23
4.2	Comparison of pH and temperature on denitrification rates	23
4.3	Cellular growth rate in high phosphate SGW	29
4.4	Cellular growth rate in SGW	29
4.5	Cellular growth rate in well 199-H4-4 with no phosphate	30
4.6	Cellular growth rate in well 199-H4-4 with phosphate	30
4.7	Cellular growth rate in well 199-D5-15 (Table A.6)	31
4.8	Cellular growth rate in well 199-D5-15 (Table A.7)	31
4.9	Slower growth rate in well 199-D5-15	32
4.10	Typical time progression of nitrate, nitrite, and acetate in SGW	32
4.11	Typical time progression of nitrate, nitrite, and acetate in well 199-H4-4	33
4.12	Typical time progression of nitrate, nitrite, and acetate in well 199-D5-15	33
4.13	2:3 stoichiometric ratio of acetate-to-nitrate	35
4.14	1:1 stoichiometric ratio of acetate-to-nitrate	35
4.15	3:2 stoichiometric ratio of acetate-to-nitrate	35
4.16	Time progression of nitrate at pH 6, 7, and 8	37
4.17	Observed pH dependencies	37
4.18	Initial and final pH	38
4.19	Time progression of nitrate at 15, 25 and 35 °C	39
4.20	Comparison of acetate and methanol for nitrate removal	40

CONTENTS (cont)

FIGURES (cont):

4.21	Large volume denitrification data	42
4.22	Final confirmation test data	43

TABLES:

3.1	Principle Equipment Used During the Treatability Test	20
4.1	Observed Denitrification Rate Contents	24
4.2	Average Nitrate Concentrations Measured in the Treatability Test Compared to the Values from the HEIS Database	25
4.3	Composition of Chemicals Added to Make a Phosphate Buffered SGW	26
4.4	Calculated Average and Standard Deviation of the Observed Specific Growth Rates	27
4.5	Estimated Annual Ray Chemical Costs for Alternative Carbon Sources with Process Flow Rate	41
4.6	Data Quality Objectives for Samples	51

210-728116
94322-042

1.0 INTRODUCTION

91322-043

Biodenitrification is the biological conversion of nitrate and nitrite to gaseous nitrogen. This document describes the procedures, results, and conclusions obtained in the bench-scale biodenitrification treatability tests at Pacific Northwest Laboratory^(a) (PNL). The tests used batch studies to determine if biodenitrification could reduce the nitrate concentration to a residual of less than 45 mg/L, the current maximum contaminant level (MCL) Federal Register, 1975. Groundwater samples were tested from two wells in 100-HR-3. These tests were conducted under the guidance of Westinghouse Hanford Company (WHC), the 100-HR-3 Groundwater Treatability Test Plan (DOE/RL-92-73), and the Treatability Study Program Plan (DOE/RL-92-48). Test procedures are found in the report entitled 100 Area Groundwater Biodenitrification Bench-Scale Treatability Study Procedures (PNL-8610). Past experiments were used to determine the range to test for each independent variable (Koegler et al. 1989; Brouns et al. 1990; Truex et al. 1992). The overall objective was to demonstrate that the performance levels (45 mg/L) for nitrate in 100 Area groundwater could be met with the biodenitrification process. The conclusions are based on groundwater samples taken from two wells chosen by WHC. In addition, the effects of the following parameters on the denitrification rate and growth rate were determined:

1. Presence of inhibitory compounds
2. Carbon limitations
3. pH dependence
4. Temperature dependence
5. Carbon source (acetate and methanol) comparison.

Values for appropriate parameters were determined, and the effects of possibly inhibitory compounds were evaluated. A final set of batch tests were performed to confirm the observed microbial growth and denitrification kinetics at the best temperature, pH, and carbon source to evaluate the site-specific reaction rate kinetics. Sludge composition and stabilization were not addressed in these procedures. Sludge characteristics as measured by total and volatile suspended solids were measured during one test to give an indication of the process sludge production.

(a) Pacific Northwest Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830.

Chromium and radionuclide uptake were also measured in the final confirmation tests to determine if the biomass would adsorb significant amounts of chromium and radionuclides.

The data will be used to further evaluate the feasibility of biodenitrification as a groundwater remediation technology for the 100-HR-3 Operable Unit and will provide information required for a pilot-scale system. In parallel to these biodenitrification tests, WHC is conducting tests of both ion exchange and chromium reduction/precipitation. The results from these lab tests will be used to determine which system, biodenitrification/chromium precipitation or ion exchange, should be further evaluated for use in remediating 100-HR-3 groundwater. This determination will be based on the performance data and minimal cost information obtained from these lab tests. A report will be issued at the conclusion of the testing to summarize the biodenitrification results. These results will be used to aid in performing the Phase 3 Remedy Design (pilot-scale) treatability study for 100-HR-3. Further details regarding an overview description should reference the document - "100 Area Feasibility Study Phases 1 and 2" (DOE-RL 1992).

1.1 SITE DESCRIPTION

1.1.1 Site Name and Location

The 100-HR-3 Operable Unit is located at the northern end of the U.S. Department of Energy's (DOE) Hanford Reservation in southeastern Washington state. The 100-HR-3 Operable Unit is very large and contains contaminants that vary widely in concentration. The primary contaminants of concern for this treatability test are 1) nitrate, 2) chromium, and 3) radioactivity in the form of gross alpha and gross beta. The only well in the 100-HR-03 Operable Unit that contains all contaminants of concern above their performance levels is 199-H4-4 in the 100-H Area. Maximum chromium concentrations are found in the 100-D area, with the well 199-D5-15 showing total chromium concentrations of 1,740 ppb. This concentration is nearly 35 times the required performance level. For further information, refer to the 100-HR-3 Groundwater Treatability Test Plan (DOE-RL 1992).

1.1.2 History of Operations

Plutonium production operations in the 100-Area produced substantial amounts of nitrate from nitric acid, dissolved chromium, and radionuclides. Waste disposal practices, such as the use of solar

evaporation basins in the 100-H Area, resulted in the discharge of substantial amounts of contaminants to the vadose zone and groundwater in the 100 Area.

1.1.3 Prior Removal and Remediation Activities

Little has been done to remove or remediate the contaminated soil and groundwater. Treatability tests for soil washing, chromium and radionuclide precipitation, and in situ vitrification are currently in progress.

2.0 CONCLUSIONS AND RECOMMENDATIONS

2.1 CONCLUSIONS

The performed tests indicate that biodenitrification is a viable technology for removing nitrate from 100 Area groundwater. Although laboratory-made simulated groundwater (SGW) gave slightly higher growth rates, actual groundwater from both well 199-H4-4 and 199-D5-15 was denitrified at similar rates. The Hanford denitrifying bacterial consortia responded to changes in temperature and pH in a manner typically observed in other denitrifying populations. Carbon limitations did not significantly affect the rates of denitrification, although carbon limitations did alter the extent of denitrification, confirming the stoichiometric equations presented in the text. As expected, acetate gave a faster rate of denitrification than methanol. Radionuclide removal was measured as the difference between gross alpha and gross beta concentrations in the liquid before and after biomass was filtered from the solution. The radionuclide removal results were mixed. Gross alpha reductions were measured to be an average of 25%, whereas gross beta reductions were measured to be only an average of 2.5%. Biological chromium removal data show chromium concentration reductions were measured to be an average of 15 $\mu\text{g/L}$ or 1.5%. In both the radionuclide and chromium data, contaminant reductions are not statistically significant.

Brief answers to the test objectives found in Section 4.2.1 of the Test Plan (DOE/RL-92-73, Rev. 0) are given below.

Determine what conditions allow native bacteria to remove nitrates below performance levels. Native bacteria were able to remove nitrates to below performance levels at temperatures between 15 and 35°C, pH from 7 to 8, using both acetate and methanol as a carbon source. At pH 6, results were mixed. Therefore, it is recommended that during remediation operations, groundwater pH is not

allowed to go below pH 6.5. Sufficient carbon source must be added to satisfy the stoichiometric requirements for nitrate and nitrite reduction.

Determine if compounds or physical conditions that would inhibit the denitrification process (e.g., the presence of biocides that may have been used in the reactor cooling loop) are present in the groundwater. Denitrification to below performance levels occurred in samples from both wells tested.

Denitrification rates in raw groundwater were insignificantly different when compared to SGW. Observed denitrification rates in raw groundwater were 80 and 95% of the rate in SGW for wells 199-D5-15 and 199-H4-4, respectively. Specific cellular growth rates were slightly slower in the raw groundwater.

Determine the optimum carbon source and dosage needed to maintain a stable biomass for denitrification (i.e., steady state operation). Two carbon sources were tested: methanol and acetate. Both carbon sources were able to reduce nitrate concentrations below the performance levels. Methanol is, by far, the industry standard. Acetate is, however, safer and gives slightly higher denitrification rates. Methanol is less expensive and produces less secondary sludge that will require disposal. Dosage requirement calculations for both compounds as a function of initial nitrate concentration are presented in Section 3.2.2. These stoichiometric dosage requirements were confirmed in the treatability tests. At the pilot scale, an additional carbon source must be added to reduce the dissolved oxygen concentration before denitrification can proceed. Without further knowledge of the final process configuration and the effects of increased safety awareness on the Hanford reservation, it would be imprudent to recommend one compound over the other. I have therefore tried to present the benefits and drawbacks of each, with the final choice of the "optimal carbon source" left until the pilot- or full-scale treatment process is better defined.

Demonstrate, on a laboratory scale, that the performance level for nitrate can be met. The performance level for nitrate was met under a variety of conditions in the raw groundwater. Only at pH 6 did no denitrification occur, and then only one of two flasks did not denitrify.

Determine the amount of chromium and radionuclides (if any) that are removed during the biodenitrification process, either by adsorption on the biomass or some other mechanism. Chromium and radionuclide concentration reductions were measured during the biodenitrification process, although these measured reductions were statistically insignificant. The measured reduction of 15

$\mu\text{g/L}$ (1.5%) for chromium was from 990 ± 80 to $975 \pm 80 \mu\text{g/L}$. Measured reduction of gross alpha was 1.8 pCi/L (25%) from an average of 7.2 ± 1.85 to 5.4 ± 1.55 pCi/L. Gross beta gave mixed results with an average measured reduction of 2.5%, from an average of 31.1 ± 2.15 to 30.3 ± 2.15 pCi/L. These reductions are in the presence of very low biomass concentrations, near 10 mg TSS/L.

Confirm denitrification kinetics. Calculated denitrification rates match very closely with the observed denitrification rates of Dawson and Murphy (1972). Also, the effects of temperature and pH match closely with literature results. Recommended operating pH is in the range from 7.0 to 7.5.

Increasing the temperature increases the denitrification rate, although in many cases there will be little control over the influent groundwater temperature. A temperature of 15°C gave a denitrification rate that was 73% of the rate at 25°C. The obtained rates were determined in the laboratory where very little inactive biomass was present, and nearly all of the biomass present was capable of denitrification. This is in contrast to a field application that may have a larger percentage of inactive biomass, especially for the fixed-film reactor types. Therefore, rates obtained in this study should be viewed as the maximum possible rate. Before a full-scale denitrification process is designed, a pilot-scale process should be operated to determine more representative denitrification rates.

Determine optimum biodenitrification configuration. It was not possible within the scope of work to meet this objective with experimental testing. Therefore, in the test procedure, the objective was to recommend bioreactor types for pilot-scale tests. A deep bed fixed-film reactor is recommended for testing at the pilot-scale. This recommendation is based more on the relatively low nitrate concentrations to be removed, ease of operation, and engineering judgement, than on the results of these tests.

Determine the amount, chemical composition (with respect to chemical additives and contaminants), and physical properties of the sludge produced by the biodenitrification process. The physical properties may include settled sludge, volume, percent solids, filter cake volume, filter cake density, percent moisture, and speed of filtration. Because of the low nitrate concentrations in the groundwater, very low concentrations of biomass were produced ($\sim 10 \text{ mg/L}$), so that very little sludge was produced during the entire test. Therefore, sludge composition and stabilization were not addressed in the procedures; however, biological solids were measured. During the final confirmation test, as a result of nitrate reduction from about 45 mg NO_3^-/L to 5 mg/L, total

suspended solids (TSS) were measured at 9.4 ± 3.1 mg TSS/L. This represents a percent solids concentration of approximately 0.001%. Characterization of sludge properties should be made at the pilot-scale since these properties will depend on the reactor configuration chosen.

2.2 RECOMMENDATIONS

It is recommended that pilot-scale tests be performed to demonstrate nitrate removal on a continuous basis using a packed bed reactor. This recommendation is based more on the relatively low nitrate concentrations to be removed, ease of operation, and engineering judgement, than on the results of these tests. The tests confirm that the Hanford denitrifying consortia will denitrify groundwater from the wells tested under the test conditions. Pilot-scale tests would give a better estimate of the denitrification rates, since laboratory rates tend to be somewhat higher than observed field rates (US EPA 1975). In addition, sludge characterization would be possible at the pilot scale since larger quantities of sludge would be generated, and the reactor configuration may influence sludge characteristics. The 100-HR-3 Groundwater Treatability Test Plan (DOE/RL-92-73 Rev. 0) recommends a pilot process flow rate of 1 to 5 gpm. Depending on the size of the final process, the raw product cost advantages of using methanol may not overcome the safety aspects of using a flammable liquid in the field. The reactor must be sized to allow complete destruction of both nitrate and nitrite to nitrogen gas with an appropriate safety factor to account for a significant fraction of inactive biomass.

3.0 TREATABILITY STUDY APPROACH

Batch studies were performed to determine if biodenitrification could meet the performance level for nitrate removal in the 100 Area groundwater, as reflected in groundwater samples from two wells. The performance level for nitrate is 45 (40 CFR 141) mg/L in drinking water; this is equivalent to 10 mg/L of nitrate nitrogen, designated as $\text{NO}_3^- - \text{N}$. The performance level for chromium (VI) and total chromium is 80 $\mu\text{g/L}$ and 100 (40 CFR 141) $\mu\text{g/L}$, respectively, while the performance levels for gross alpha and gross beta are 15 (40 CFR 141) pCi/L and 40 (WHC 1988) pCi/L, respectively. These tests were conducted under the guidance of the 100-HR-3 Groundwater Treatability Test Plan, DOE/RL-92-73 Rev. 0, using groundwater from 100-HR-3 and the Hanford denitrifying consortium.

3.1 TEST OBJECTIVES AND RATIONALE

Specific test objectives are listed below:

- Determine if inhibitory compounds are present - This objective was accomplished by comparing denitrification rates in 100-HR-3 groundwater to denitrification rates in an SGW under identical conditions. Because of the possibility that the 100 Area groundwater may contain compounds that inhibit microbial denitrification, tests were run to determine if the rate and extent of denitrification in the groundwater was comparable to the rates commonly expected when no inhibitory compounds were present.
- Determine the extent to which carbon limitations affect denitrification - This was done to ensure that nitrate was indeed the rate limiting nutrient and to determine the effects of carbon limitations on denitrification rates. Since the MCL for nitrate is 45 mg/L, a pilot-scale system may be operated in a carbon limited manner and still remove enough nitrate to effectively remediate the effluent water. At the pilot-scale, nitrite will need to be monitored to ensure that the performance level for nitrite is not exceeded.
- Determine denitrification rates at pH values 6, 7, and 8 - The solution pH increases as a result of the biochemical reactions for biodenitrification. Depending on the buffering capacity of the groundwater, this increase may be large or small and may affect denitrification rates. In addition, information on the effect of pH on denitrification rates may play a significant role in integrating chemical and biological treatment at this site since pH control plays an important role in chemical precipitation. Initial measurements of groundwater pH were between 7.6 and 8.0.
- Determine the effect of temperature on the rate of denitrification. Even with a relatively stable groundwater temperature, an ex-situ process at the Hanford site may expect certain temperature fluctuations throughout the year. This objective, specifically, is to determine denitrification rates at 15°C, 25°C, and 35°C. Generic rate expressions that account for the effect of temperature on denitrification rates exist, but the constants need to be determined under site-specific conditions. The groundwater temperature in the 100 Area was typically in the range 17 to 20°C.
- Determine carbon source and dosage - The role of the carbon source is important in determining denitrification and biomass production rates. The carbon sources that will be compared are acetate and methanol. Methanol is an industry standard because of its cost, but acetate may give faster denitrification rates. Dosage was determined by analyzing observed yield values after removing nitrate and producing biomass. The desirable carbon source would be inexpensive and would support a high denitrification rate while producing a small amount of biomass. Initial dosage was determined from Equation 5 or 6 in Section 3.2.2; these tests gave data to predict the amount of carbon source required to remove a specific amount of nitrate from groundwater.

Final confirmation tests that need to be performed are listed below:

- Confirm that performance levels could be met - After optimal values for the parameters given above have been chosen, and the effects of possibly inhibitory compounds have been evaluated, a final set of integrated batch tests were performed to evaluate the site-specific reaction rate kinetics and determine if denitrification could reach the desired performance levels of 45 mg/L in 100 Area groundwater.
- Determine the amount of chromium and radionuclide adsorption to biomass - Although some information is available on the extent of chromium uptake by the Hanford denitrifying consortia, the information on the extent of radionuclide adsorption is limited.
- Recommend bioreactor types for pilot-scale tests - Bioreactor types that should be evaluated at the pilot-scale are recommended based on denitrification rates observed in these tests. The recommendation does not include information about costs.

3.2 EXPERIMENTAL BACKGROUND

This section gives some technical background for the process of biodenitrification and the process parameters that affect the rate of denitrification.

3.2.1 Experimental Principles

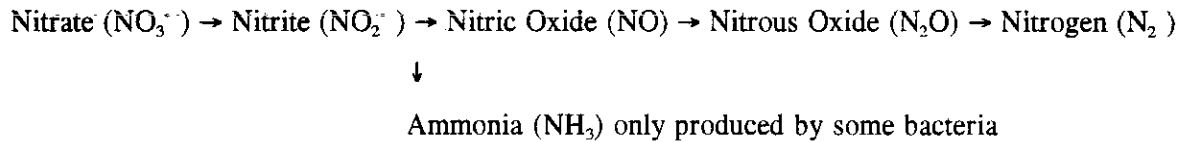
The fundamental principle of bioremediation is the biological degradation of unwanted compounds into more inert or desirable compounds. For example, biodegradation of a gasoline spill in the presence of air would produce carbon dioxide, a gas found in low concentrations in ambient air. In the absence of molecular oxygen (O_2), other substances can be used by bacteria to degrade organic carbon. One such substance is nitrate. Degradation of nitrate by the microbial process of denitrification produces inert nitrogen gas through the reaction series in Equation 1.



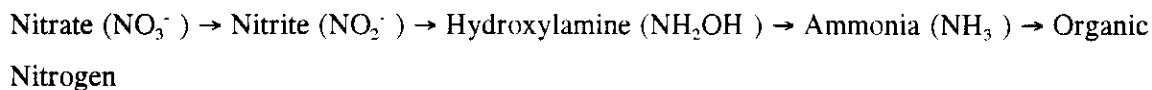
The Hanford consortia has been shown to reduce both nitrate and nitrite. A consortia undergoing the denitrification process rarely produces ammonia, since ammonia has a high chemical energy and is a valuable nutrient source for bacteria. To illustrate this, it is useful to examine the assimilatory (biomass producing) and dissimilatory (energy producing) pathways. It can be seen that under denitrifying conditions, produced ammonia can be directly incorporated into organic nitrogen

for cell proteins and other components. About 90% of all nitrate converted goes through the dissimilatory pathway. Of the small amount of ammonia that may be produced, most will quickly be assimilated into biomass.

Dissimilatory Pathway:



Assimilatory Pathway:



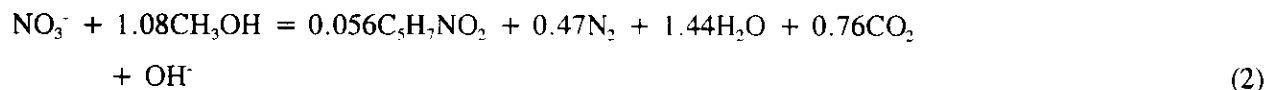
3.2.2 Carbon Limitations

Stoichiometric relationships for nitrate removal were the basis for adding a carbon source.

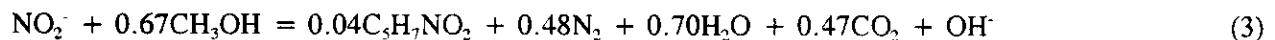
Both acetate and methanol additions were calculated by

- measuring initial nitrate and nitrite concentrations
- using the stoichiometric relationships (Eq. 2 to 6) that incorporate dissimilatory nitrate/nitrite reduction, biomass synthesis, and the scavenging of soluble oxygen. These relationships (US EPA 1975) are averages for many complex metabolic reactions and as such are approximations of what will be observed with the Hanford consortia.

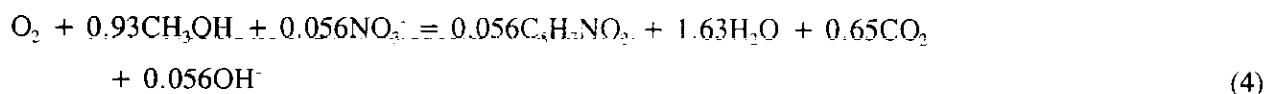
Overall Nitrate Removal with Methanol



Overall Nitrite Removal with Methanol



Overall Oxygen Removal with Methanol



When combined, these stoichiometric relationships allow methanol requirements to bioremediate nitrate and nitrite to be calculated. An additional factor of 1.5 has been included to insure sufficient carbon source to deplete nitrate. At the pilot scale, this safety factor would be set to 1.0 since adding too much methanol may encourage sulfate reducing bacterial growth.

Overall Methanol Addition

$$C_m = 1.5 (0.56\text{NO}_3^- + 0.35\text{NO}_2^- + 0.93\text{DO}) \quad (5)$$

where

C_m = required methanol concentration, mg/L

NO_3^- = nitrate concentration to remove, mg/L

NO_2^- = nitrite concentration to remove, mg/L

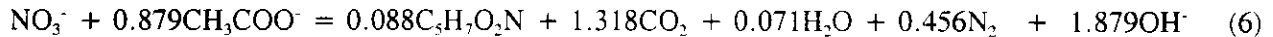
DO = dissolved oxygen concentration to remove, mg/L

The dissolved oxygen must be taken into consideration since oxygen is a more energetically favorable electron acceptor. If, for example, the dissolved oxygen were ignored and only enough carbon source were added to remove nitrate, the bacteria would still remove the oxygen first and then proceed with denitrification. In this case, the carbon source may be depleted before all the nitrate was consumed.

Examination of Equation 5 will show that in the laboratory tests, flasks were sparged with helium to remove oxygen so that oxygen had no influence on the methanol requirement. Pilot-scale designers and operators will have to measure the dissolved oxygen and nitrate concentration and add enough carbon source to remove both. In addition, effluent monitoring for nitrate and nitrite should be used to "fine tune" carbon dosage to remove the nitrogen containing compounds without adding excess carbon source.

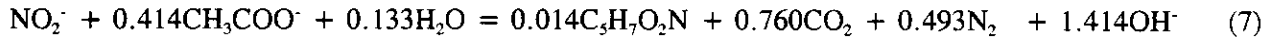
Acetate was used in the form of sodium acetate. Although acetate provides a faster denitrification rate, its use is less common on a larger scale because of cost considerations. Acetate addition was calculated based on Equation 6 adapted from Table IV of McCarty et al. (1969) and will provide a safety factor of 1.5 in the acetate additions to ensure a sufficient carbon source to deplete available nitrate and oxygen. It can be seen that more biomass is produced per mole of nitrate when using acetate as the carbon source.

Overall Nitrate Removal with Acetate

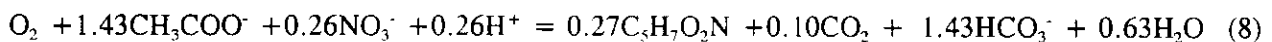


The reaction of nitrite and oxygen in the presence of acetate was developed with the half reaction method from Grady and Lim (1980).

Overall Nitrite Removal with Acetate



Overall Oxygen Removal with Acetate



Combining Equations 6 through 8 gives the overall acetate addition for removing nitrate, nitrite, and oxygen, and changing the units to mg/L gives a useful equation (9) for predicting the required acetate dosage.

$$C_a = 0.84\text{NO}_3^- + 0.53\text{NO}_2^- + 2.64\text{DO} \quad (9)$$

where C_a = initial acetate concentration, mg/L

As with methanol, a safety factor of 1.5 was included to ensure complete nitrate degradation. At the pilot scale, a safety factor near 1.0 is recommended since adding an excess carbon source above the required minimum may lead to unwanted sulfate reduction and increased cost. During the treatability tests, the overall acetate addition was calculated using Equation 10.

Overall Acetate Addition

$$C_a = 1.5 (0.81 \text{ NO}_3^-) = 1.22 \text{ NO}_3^- \quad (10)$$

3.2.3 pH Dependence

The highest denitrification rates are found between a pH of 7.0 to 7.5 (US EPA 1975). Lower denitrification rates occur outside of this range. The typical range for the effects of pH on the percent of maximum denitrification rate is shown in Figure 3.1.

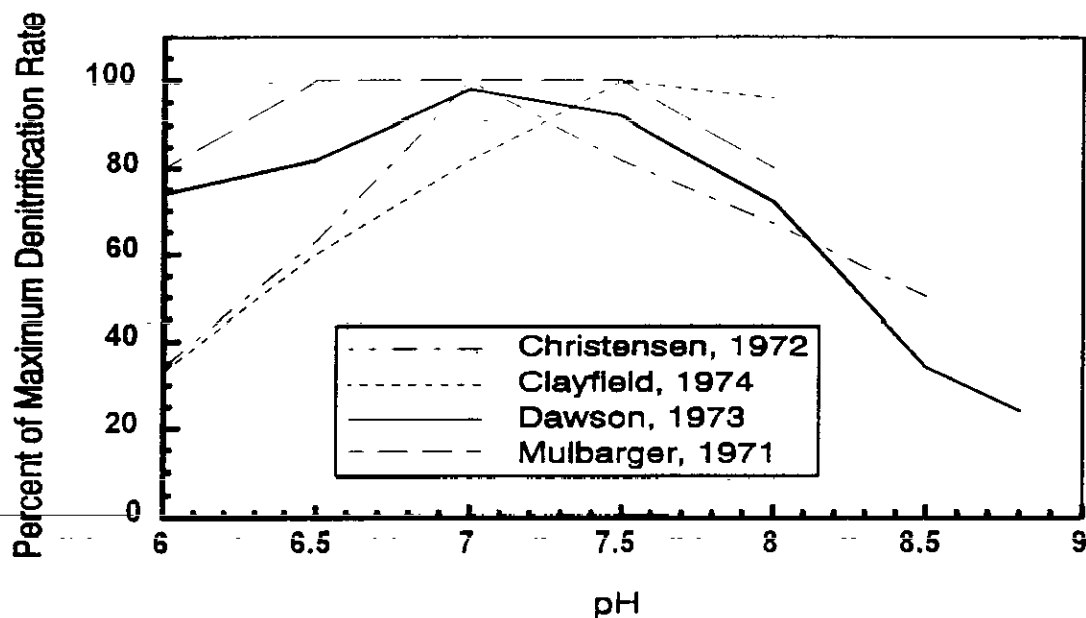


Figure 3.1. pH Effects on percent of maximum denitrification rate observed by others. Adapted from EPA (1975).

3.2.4 Temperature Dependence

The temperature dependence of the denitrification rate was fitted with a least squares fit of a logarithmic transformation (Dawson and Murphy 1972) with an Arrhenius' Law model of the form:

$$k = k_0 e^{-(E/RT)} \quad (11)$$

where

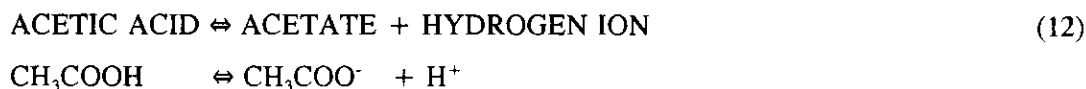
- k_0 = frequency factor
- E = activation energy (cal g-mole⁻¹)
- R = universal gas constant (cal g-mole⁻¹ °K⁻¹)
- T = absolute temperature (°K)

Dawson and Murphy obtained a value for E of 16,000 (cal g-mole⁻¹). Because the coefficients represent overall averages of many complex individual metabolic reactions, this test procedure gave an estimate, but could not precisely define the coefficients k_0 and E . The groundwater in the 100 Area typically ranges between 17 and 20°C.

3.2.5 Acetate and Methanol Comparison

Since both acetate and methanol are suitable carbon sources for denitrifying groundwater, the four primary issues related to the choice of a carbon source are 1) cost, 2) safety, 3) sludge production, and 4) operational efficiency.

Acetate is the base ion, or deprotonated form, of acetic acid as shown by



Acetate was chosen as a test compound because it is non-flammable, is easy to measure, gives good denitrification rates, and helps maintain pH. Methanol is the industry standard because of the cost-benefit ratio at very large scales, but it gives a somewhat slower denitrification. According to data obtained in the treatability tests, the use of acetate, rather than methanol, would result in denitrification rates that would be approximately 20% faster. This rate increase would reduce the hydraulic residence time required for complete denitrification, thus resulting in a smaller bioreactor to process the same groundwater volumetric flow rate.

The February 22, 1993, Chemical Marketing Reporter indicates that the price of methanol was \$0.154/Kg methanol, and acetate was \$0.727/Kg acetic acid. Calculations based on the stoichiometric ratio of each carbon source indicates that the cost for nitrate removal with methanol would be \$0.086/Kg nitrate, whereas the cost for acetate would be \$0.599/Kg nitrate. The cost ratio of these two carbon sources is 6.96, indicating that acetate would be nearly seven times more expensive in raw chemical costs as compared to methanol. Because of the relatively small amount of nitrate present in the groundwater, however, this cost ratio may be somewhat misleading. Estimated raw chemical costs were calculated for a nitrate removal of 40 mg NO₃⁻/L at four process flow rates (Table 4.2).

From a safety standpoint, acetate is by far the safer of the two carbon sources. Methanol is flammable with a flashpoint of 52°F (13.9°C); therefore, special non-sparking tools and equipment, in addition to other safety precautions, are required to use methanol. The flashpoint for acetic acid is listed on the MSDS as "none." Acetate is usually supplied in the form of acetic acid. Acetic acid is

flammable and corrosive at very high concentrations, although at typical concentrations used, flammability is not an issue.

Comparing sludge production between Equations 2 and 7 shows that acetate will produce approximately 57% more sludge because of the higher biomass yield. In a 1000 gpm full-scale plant operating 365 days a year and removing 40 mg/L NO_3^- , methanol would produce about 17,000 lb of undigested sludge, while acetate would produce 27,000 lb. In a smaller unit of 10 gpm the estimated sludge production is 170 lb for methanol and 270 lb for acetate. At this scale, the difference in sludge production is small.

Overall, the balance of cost versus safety issues for methanol does not become significant until large scale (> 100 gpm) process units are reached.

3.2.6 Scale-up Issues

The primary scale-up issues for a fixed film system are the ability to reliably estimate the total amount of biomass that will be attached to the packing in the reactor and the ability to minimize the amount of start-up time required to bring the unit on line after a system upset.

To estimate the amount of biomass attached to the reactor packing, previous work with packed bed denitrifying units will be used (US EPA 1975). In addition, a safety factor for a hydraulic retention time of greater than 2.0 is recommended. In addition, laboratory rates should be viewed as high, since field systems may have a large fraction of "inactive" volatile suspended solids (US EPA 1975).

The start-up time can be minimized by providing a packing material that maintains a large amount of biomass with a minimal amount of sloughing. This usually requires a rough or porous surface that allows denitrifying bacteria to enter the pore spaces, thus minimizing bacterial washout during start-up. This type of reactor packing can also increase the amount of biomass that is retained in the reactor.

An additional scale-up issue is the accumulation of nitrite as a natural product of nitrate reduction. Both nitrate and nitrite concentrations should be monitored carefully. The reactor residence time and the amount of carbon source added should allow for nitrite degradation. In

addition, data obtained in these treatability tests indicate that at pH 6, nitrate degradation was slow, and nitrite degradation was inhibited; therefore, a pH controller should be installed to maintain the pH in the range of 7 to 7.5.

3.2.7 Phosphorous Requirements

Phosphorous is a member of the group of chemical elements commonly called micronutrients. These elements are required for microbial growth, though in far smaller amounts than carbon, nitrogen, hydrogen, and oxygen. Hydrogen and oxygen exist in great abundance as the components of water. In this application, a carbon source, acetate or methanol, will be added to bioremediate a nitrogen source, nitrate. Thus all the primary components for bioremediation will be present in the planned tests. In an anoxic environment, phosphorous is required in the approximate molar ratio of 300:1 carbon:phosphorous by the microbial cell to produce important biological substances such as genetic material (nucleic acids) and the cell wall (phospholipids). In some cases, a scarcity of phosphorous can limit cell production, which in turn limits the denitrification rate. Phosphate was added to groundwater samples with the carbon source in the ratio of 0.05 mg PO_4^- per mg acetate or methanol.

It should be noted that while the concentration of phosphorous is known for biological cell requirements, other factors, including chemical precipitation, contribute to the loss of available phosphorous concentrations. In continuous treatment, it is essential in maintaining target treatment efficiency to maintain available phosphorous concentrations. This typically is effected by measuring soluble ortho-phosphate during start-up and during changes in influent quality. Thus, the ratio of carbon:phosphorous should be considered a target ratio that requires monitoring and may require adjustment for continuous, efficient, and stable operations.

3.2.8 Nitrite Production

In Equation 1, it can be seen that nitrite, NO_2^- , is an intermediate of the pathway from nitrate, NO_3^- , to nitrogen gas, N_2 . Nitrite has a maximum contaminant level (MCL) of 10 mg NO_2^-/L (40 CFR 59569). Typically, a microbial consortia that can degrade nitrate can also convert nitrite to nitrogen gas. The Hanford consortia has been shown to degrade nitrate through nitrite to nitrogen gas in this and other studies, although this information has not been published.

In biological reactors containing a microbial consortia capable of nitrite reduction, two primary conditions can cause an accumulation of nitrite in the process. In batch reactors, the presence of nitrite at the end of an experimental run indicates that either 1) the batch test was not run long enough to allow the nitrite to be converted to nitrogen gas, or 2) the amount of carbon source added to the flask was not sufficient to degrade both the nitrate and nitrite.

For a continuous flow pilot-scale system, two analogous conditions can cause the production of nitrite in the effluent. These conditions are:

1. The hydraulic retention time is too short to allow the transformation of produced nitrite.
2. The concentration of the organic carbon source has been depleted so that no further microbial transformation of nitrate or nitrite will occur.

3.2.9 Hanford Denitrifying Consortia

A denitrifying consortium was obtained from Hanford groundwater (Koegler et al. 1989) and has been shown to remove nitrate to concentrations less than 45 mg/L, the current MCL. The consortium was initially obtained for tests to degrade nitrate in a condensate stream from Hanford's UO₃ Plant and was subsequently found to degrade carbon tetrachloride and nitrate simultaneously. Koegler et al. (1989) determined that over the pH range of 7.95 to 11.6, a pH of 8 gave the highest rate of denitrification. This result is not surprising given the range of pH examined. These tests were performed under continuous culture conditions, with residence times of 5, 8, 12, and 20 days. The influent nitrate concentration for each test was 1500 mg NO₃⁻, as compared to the typical nitrate concentrations of 140 mg/L found in the 100 Area groundwater. An order of magnitude cost estimate was made for the pilot-scale biological denitrification of the UO₃ Plant condensate effluent.

Brouns et al. (1990) found that a fluidized bed bioreactor (FBR) gave volumetric denitrification rates 10 to 20 times higher than those obtained in a continuous culture and that 99% of nitrate at concentrations of 400 mg/L could be reduced with a residence time of 8 h. This was because of the order-of-magnitude increase in the amount of biomass present in the reactor as a result of the presence of an attachment medium. The report focuses on results obtained from the biological destruction of carbon tetrachloride, although some screening work on chromium (VI) inhibition was performed. It was found that at Cr(VI) concentrations of 0.11 ppm, the onset of denitrification was delayed. At Cr(VI) concentrations of 4.1 and 40 ppm, denitrification was not observed to occur.

Specific denitrification rates, as a function of volatile suspended solids (VSS), averaged from 9 to 14 mg NO₃⁻(g VSS h)⁻¹. These values were obtained at 30°C. The average observed yield for nitrate was 0.97 mg NO₃⁻ (mg VSS)⁻¹ and a range of 3.3 to 10.8 mg acetate (mg VSS)⁻¹ was reported. These results should be viewed with some amount of caution since the tests were carried out in a fed-batch system under famine conditions.

3.3 EXPERIMENTAL DESIGN AND PROCEDURES

The primary goal of this work was to provide information on the applicability of biodenitrification for treating 100-HR-3 groundwater. Microorganisms grown in batch culture were used to determine the effects of various parameters and operating conditions on the denitrification rate. The principal parameter of interest was determining if any unknown inhibitory agents that would prevent biodenitrification from occurring were present in 100-HR-3 groundwater. All experiments were performed at 25°C, with the exception of 1) the tests to determine temperature dependency, 2) the large volume denitrification, and 3) the final confirmation test that were performed at 20°C to better represent rates that would be observed in the field. The pH of all experiments was that of the raw groundwater, with the exception of those tests to determine the effect of solution pH. The flask of composite groundwater at pH 7.0 was used as the standard to compare all other treatments. Carbon loading was calculated based on the measured nitrate concentration according to equation 5 or 7 in Section 3.2.2. Detailed procedures are given in Peyton and Martin (1993). From the procedures document, Section 3.4.3 (Determining pH Dependence) is given below as an example.

1. Measure nitrate and nitrite concentration and pH according to methods given in Appendix A on a composite groundwater sample made from equal volumes of water from each of two wells.
2. Measure pH in groundwater according to method given in Appendix A (Peyton and Martin (1993)).
3. Calculate acetate concentration required to deplete nitrate and oxygen based on Eq. 4.
4. Add 300 mL groundwater to six 500-mL shake flasks.
5. Add 5.0 x 10⁻⁴ molar phosphate buffer to all flasks.
6. Raise pH in two flasks to pH 8 using sterile 1 M NaOH.
7. Lower pH in two flasks to pH 6 using sterile 1 M HCl.

8. Adjust pH in two flasks to pH 7 using either sterile HCl or NaOH as required.
9. Sparge the liquid of each flask with sterile helium to remove atmospheric oxygen.
10. Add 0.1 mL ($\sim 2 \times 10^6$ cells/mL) Hanford denitrifying consortia inoculum to each flask.
11. Add calculated amount of sterile acetate to each of the shake flasks.
12. Incubate in a dark shake chamber at 150 rpm at room temperature.
13. Aseptically sample each flask for nitrate, nitrite, acetate, and denitrifying cell numbers (MPN) according to methods given in Appendix A (Peyton and Martin (1993)).
14. Sample at 4, 8, and 12 h.
15. Determine final pH on remaining liquid after final sampling.
16. If no significant statistical difference (95% confidence interval) is observed in the rate or extent of denitrification between the different pH flasks, it will be concluded that no pH effects were measured in the sample. In the more likely case that pH does have an effect on denitrification rates, data will be used to determine the pH-dependency.

0645728746

3.4 EQUIPMENT AND MATERIALS

The principal piece of test equipment was a commercially available rotary shaker/incubator that is temperature controlled. This was used to maintain the chosen temperature at a constant value throughout the length of the tests. Custom-made Erlenmeyer flasks (Figure 3.2) containing the culture media were inoculated with the Hanford Consortia, kept at a set temperature, and shaken at 150 rpm to ensure complete mixing during the individual 1 to 2 week tests.

Other equipment is listed in Table 3.2.

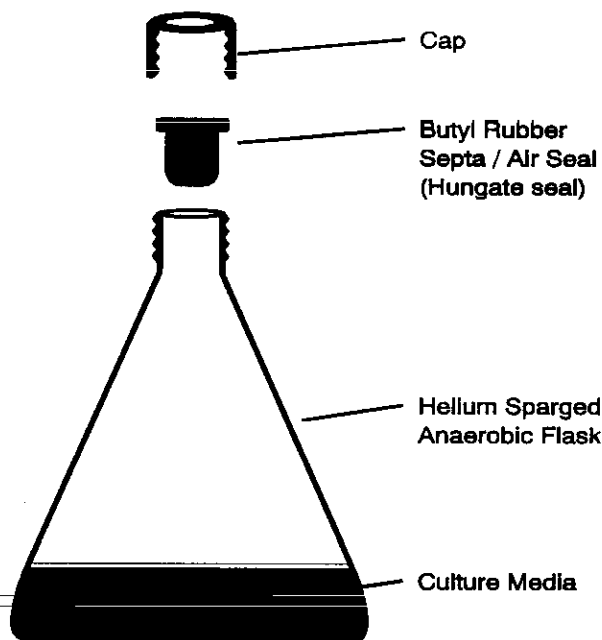


Figure 3.2. Custom Made Anaerobic Flasks were used to Grow the Denitrifying Bacterial Culture Under Anoxic Conditions.

3.5 SAMPLING AND ANALYSIS

Sampling and analysis was performed in accordance with the "100 Area Groundwater Bionitrification Bench-Scale Treatability Study Procedures" (Peyton and Martin 1993) with deviations given in Section 3.7 of this document.

3.6 DATA MANAGEMENT

The QA parameters for reproducibility of duplicates and recovery of National Institute of Standards Testing (NIST) nitrate standards were met before the data were accepted. Data management was performed by entering raw analytical data into Microsoft Excel spreadsheets.

Table 3.1. Principle Equipment Used During the Treatability Test.

Item	Manufacturer
environmental rotary shaker	New Brunswick
ion chromatograph	Dionex
pH meter, model 250 A	Orion
gas chromatograph, 5890 Series II	Hewlett Packard
custom anaerobic flasks, 500 mL, Hungate-type anaerobic seal	Bellco, Inc.
fermentor	New Brunswick
autoclave	Consolidated Machine Corp.
refrigerator	Kenmore
environmental chamber	Bally Engineered Structures, Inc.
balance, AE 160	Mettler
laminar flow hood	Labconco

3.7 DEVIATION FROM THE WORK PLAN

Deviations from the work plan are listed below.

1. Sampling times used to monitor the experimental progress were adjusted to provide a clearer picture of the microbial process after it was determined that the groundwater required a longer lag phase than the SGW.
2. Only total chromium was monitored during the final confirmation tests. This was because environmental compliance was to be based on total chromium and not on individual concentrations of chromium (III) and (VI).

946322.0132

3. Suspended solids measurements were tried with the filters recommended by standard methods, however, since the suspended solids concentration was so low and the total amount of sample available for filtration was small, a finer (0.2 micron) pored filter was used to obtain measurable amounts of biomass.
4. Test procedures that called for incubating the cultures at room temperature were instead incubated at 25°C to give better temperature control.

4.0 RESULTS AND DISCUSSION

This section presents the test results and discusses the implications of each result as it pertains to the design and operation of a pilot biodenitrification unit. Raw data are found in Appendix A.

4.1 DATA ANALYSIS AND INTERPRETATION

The test results indicate that biological denitrification is a potentially effective treatment for removing nitrate in the 100 Area. No significant differences were found between the observed denitrification rates of SGW and the rates in either of the wells tested. Although the calculated denitrification rates are similar, cell concentration data indicate that a longer lag phase may be required for the bacteria to adjust to water from well D5-15. The growth and denitrification rates depended on pH and temperature in much the same way that has been observed and documented in the scientific literature. At pH 6, one shake flask had no growth or denitrification, while the other flask denitrified after a lag phase. Therefore, the data shown for pH 6 are from the flask that showed denitrification activity.

Denitrification rate constants were calculated by an integral method, using data found in Appendix A, to reduce the variability in observed rate constants; however, the results still have a marked standard deviation. This is in part because relatively few tests were run for each condition and because of variability in measuring the low biomass concentrations. Because of the low biomass concentrations and the small amount of sample volume available, volatile suspended solids were calculated using equation 5 for methanol and equation 7 for acetate found in section 3.2.2.

Therefore, the average observed rate and its corresponding standard deviation will be used to compare differences between observed denitrification rate constants.

Figure 4.1 shows that denitrification rates in the raw groundwater from wells H4-4 and D5-15 were insignificantly different than rates observed in SGW. In addition, Figure 4.1 shows the effects of different stoichiometric ratios of acetate/nitrate and the observed denitrification rate using methanol ("HD MeOH") as a carbon source. Using methanol as the carbon source gave an observed rate constant that was approximately 20% lower than that using acetate, although the difference is not statistically significant. The symbol "HD" indicates that equal volumes of water from the two sources (wells 199-H4-4 and 199-D5-15) were mixed in a composite sample, while the symbols "2/3", "1/1", and "3/2" indicate the acetate-to-nitrate stoichiometric ratio. Finally, Figure 4.1 shows that the acetate-to-nitrate ratio had little effect on the denitrification rate. However, it will be shown later that while not limiting the rate, the acetate-to-nitrate ratio did determine the extent of nitrate conversion.

Figure 4.2 shows the effects of both pH and temperature on the denitrification rate constant. It can be seen that pH 7 and 8 gave higher denitrification rates, while pH 6 was slower. One flask run at pH 6 showed no denitrification, while the other flask at pH 6 gave the slowest rates observed during the treatability tests. Temperature had the most significant effect on denitrification rates of any of the variables tested. At the low temperature of 15°C, the denitrification rate was 73% of the rate at 25°C. Overall, with the exception of the tests run at 35°C and tests run at pH 6, the average denitrification rates were fairly consistent (Table 4.1).

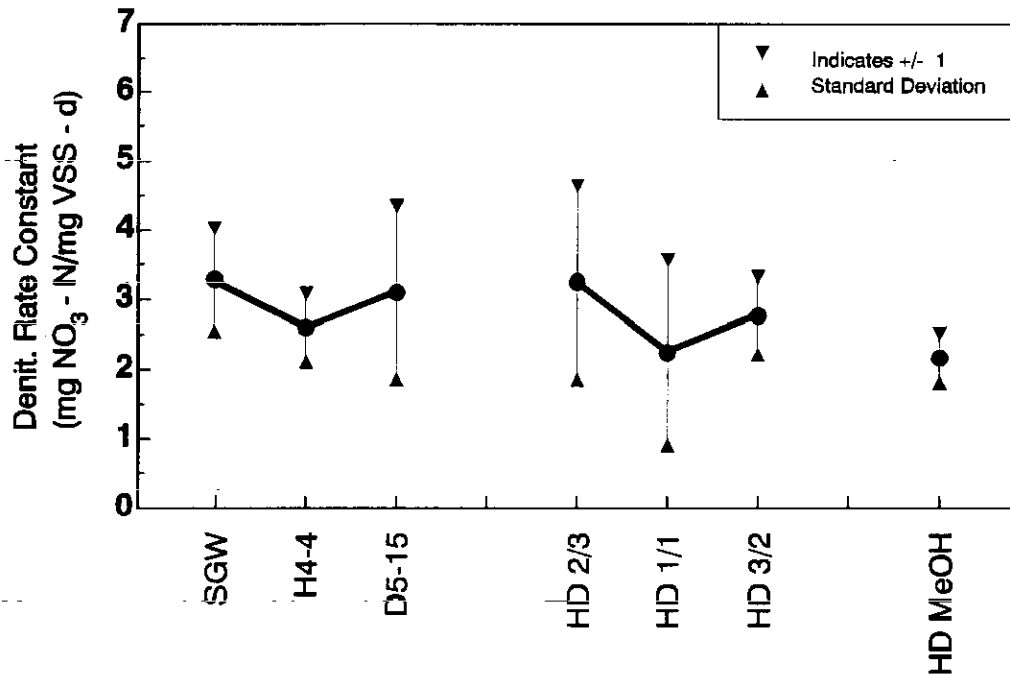


Figure 4.1. Comparison of Observed Denitrification Rates for SGW, Raw Well Water (H4-4 and D5-15), and Equal Volume Composite Samples. See Text for Symbol Explanation.

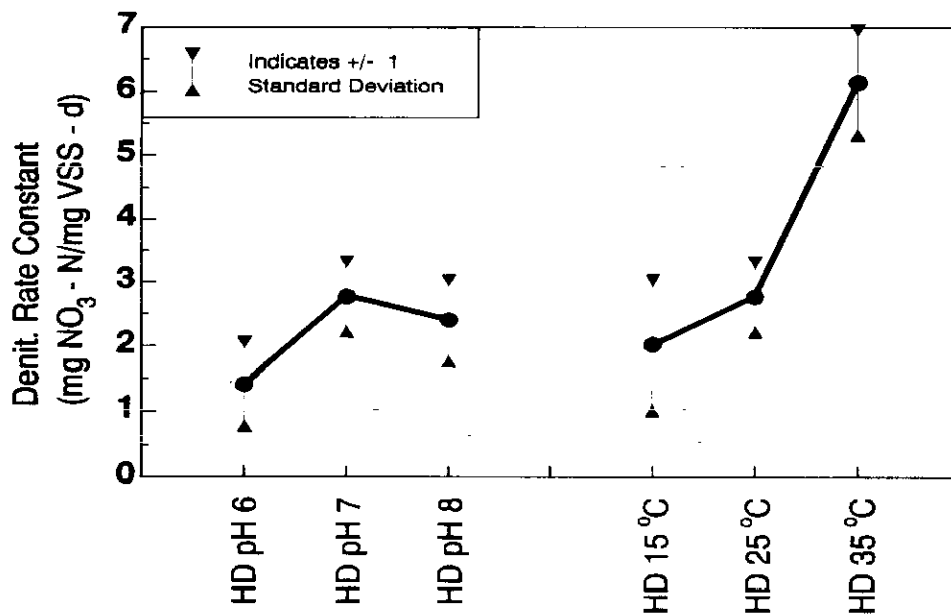


Figure 4.2. Observed Effect of pH and Temperature on Denitrification Rate Constants for Acetate

Table 4.1. Observed Denitrification Rate Constants and Standard Deviations.

<u>Test Condition^(a)</u>	<u>Carbon Type</u>	<u># Replicate Flasks</u>	<u>Samples in Rate Calc.</u>	<u>Temperature</u>	<u>pH</u>	<u>Data Table # 's</u>	<u>Rate Constant (mg NO₃-N/mg VSS-d)</u>	<u>Standard Deviation</u>
SGW ^(b)	Acetate	2	18	25°C	6.9	A. 1-2	3.25	0.74
Well H4-4	Acetate	2	20	25°C	7.9-8.1	A. 3-4	2.60	0.49
Well D5-15	Acetate	2	13	25°C	7.8-8.0	A. 5-7	3.10	1.24
HD pH 6	Acetate	1 ^(c)	6	25°C	6.0	A. 8	1.42	0.64
HD pH 7	Acetate	2	17	25°C	7.0	A. 9	2.77	0.55
HD pH 8	Acetate	2	34	25°C	8.0	A. 10-11	2.40	0.63
HD 15°C	Acetate	2	10	15°C	7.8	A. 12	2.03	1.01
HD 25°C	Acetate	2	17	25°C	7.0	A. 13	2.77	0.55
HD 35°C	Acetate	2	11	35°C	7.8	A. 13	6.15	0.82
HD 2/3	Acetate	2	7	25°C	7.8	A. 14	3.25	1.38
HD 1/1	Acetate	2	10	25°C	7.8	A. 15	2.24	1.33
HD 3/2	Acetate	2	17	25°C	7.0	A. 9	2.77	0.55
HD MeOH	Methanol	6	69	25°C	7.8	A. 17-23	2.17	0.35

(a) = The symbol "HD" indicates that equal volumes of water from well 199-D5-15 and 199-H4-4 were combined for this test.

(b) = Only one flask at pH 6.0 showed any denitrification activity.

4.1.1 Analysis of Waste Stream Characteristics

No special groundwater analytical characterization was performed as part of this treatability test. Data available from the Hanford Environmental Information System (HEIS) database were determined to be sufficient to perform the screening tests, although a more thorough characterization should be made once a specific well or set of wells is selected for the pilot-scale tests.

4.1.2 Analysis of Treatability Study Data

Conclusions are presented in Section 2.0 of this report. Further characterization of the contaminants of interest and some wet chemistry parameters should be made during the pilot-scale treatability tests. It is worthwhile to note that the average measured nitrate concentrations determined for raw groundwater as a result of this treatability test are in the range reported (Table 4.2) from the HEIS database for well 199-H4-4 (Appendix D).

Table 4.2. Average Nitrate Concentrations Measured in the Treatability Test Compared to the Values from the HEIS Database.

<u>Well</u>	<u>HEIS database</u>	<u>Measured treatability test average (mg/L)</u>
199-D5-15	Not Reported	45.5
199-H4-4	26 to 110	81.4

4.1.2.1 Presence of Inhibitory Compounds. The primary goal of the treatability tests was to determine if inhibitory compounds that could prevent the use of biological denitrification as a treatment method were present in the groundwater from each area. The determination of inhibition was based on the observed average specific growth rate and the denitrification rate constant. SGW was used as a "control" to determine maximum expected denitrification rates. The composition of the SGW is given in Table 4.3. The specific growth rate of the bacteria is calculated as the slope of the best-fit linear regression, on a log-linear graph, through the cell concentration data points after the initial 12 to 24 h lag phase. This method for determining the specific cellular growth rate is valid only during the log growth phase, i.e., the period of rapid cell growth that typically follows the lag phase, and does not apply after the bacterial culture has reached the stationary phase. Therefore, data obtained during the lag or stationary phase is not used when calculating the specific growth rate.

Table 4.3. Composition of Chemicals Added to Make
a Phosphate Buffered Simulated Groundwater^(a)

<u>Compound</u>	<u>mg/L</u>	<u>M</u>
Na ₂ SiO ₃ ·9H ₂ O	4.55E+02	1.60E-03
Na ₂ CO ₃	1.60E+02	1.51E-03
Na ₂ SO ₄	1.33E+02	9.38E-04
KOH	2.00E+01	3.57E-04
MgCl ₂ ·6H ₂ O	2.15E-01	1.06E-06
CaCl ₂ ·2H ₂ O	1.48E-02	1.00E-07
KH ₂ PO ₄	6.80E+01	5.00E-04
NaCl	3.30E+01	5.65E-04
pH	7.0	

(a) Based on Analysis of Sulfate and Chloride of Well 199-D5-15.
Other Trace Compounds are Based on the SGW used by Brouns et al. 1990.

Figure 4.3 shows that the number of bacterial colony forming units (CFU) increases for duplicate experiments in a very high phosphate buffer concentration (13,600 mg KH₂ PO₄/L). Table A.1 provides CFU data. This concentration of phosphate was reduced to allow ion chromatographic analysis of nitrate and to prevent possible calcium or magnesium phosphate precipitation. Subsequent SGW formulations were made as written in Table 4.3 using only 68 mg KH₂ PO₄/L. Figure 4.4 gives the bacterial concentration of CFU over time for SGW with 68 mg KH₂ PO₄/L. Figures 4.5 to 4.9 give CFU/mL over time for the actual groundwater (data in Tables A.3 to A.7). It can be seen that cell concentrations increased with time under all conditions. Figures 4.3 and 4.5 each show a data point that was taken after the bacterial culture had reached the stationary phase, i.e., at 101 h on both figures. These data points were not used to calculate specific growth rate. Cell concentrations appear to be lower than expected, but may be due to cells sticking together during the cell counting analyses. Groundwater from the 100-D area may have longer lag phase to biodenitrification than SGW.

The average specific cellular growth rates and standard deviations calculated from these growth curves are given in Table 4.4.

Table 4.4. Calculated Average and Standard Deviation of the Observed Specific Growth Rates.

Water source	Average specific growth rate (1/h)	Standard deviation
SGW	0.46	0.17
Well 199-H4-4	0.33	0.22
Well 199-D5-15	0.14	0.16

It can be seen that the specific growth rate between the SGW and well 199-H4-4 decreases minimally, whereas bacteria grown in water from well 199-D5-15 had a lower specific growth rate. As a result of the limited number of tests and variability of the test results, especially for well 199-D5-15, the 95% confidence interval overlaps for all values of the average specific growth rate. Therefore, at the 95% confidence level, none of the specific growth rates are significantly different.

Well 199-D5-15, at approximately 45 mg NO₃⁻/L, has the lowest nitrate concentration of either well 199-H4-4 or the SGW. This, however, is not expected to be the rate limiting factor since literature data (US EPA 1975) indicate that the rate of biodenitrification is unaffected by the nitrate concentration down to concentrations of approximately 9 mg/L nitrate. At 9 mg/L, the specific growth rate is approximately 90% of the maximum specific growth rate. Below 9 mg/L, nutrient limitations may become dominant in determining the denitrification rate. The Monod half-saturation coefficient typically falls between 0.5 and 1 mg/L (US EPA 1993). Therefore, if significant, the lower specific growth rate in well 199-D5-15 may be due to some other form of inhibition. Typical concentrations for the onset of chromium inhibition in a chromate resistant strain is near 75,000 ppb chromium (Yamamoto et al. 1993), although it would likely be lower in the Hanford consortia used in

these tests. With nitrate concentrations measured at approximately 45 mg/L, the D5-15 groundwater is already at the nitrate performance level and may not need nitrate removal.

Figures 4.10 through 4.12 show the typical time progression of a biodenitrification experiment for SGW (Figure 4.10), well 199-H4-4 (Figure 4.11), and well 199-D5-15 (Figure 4.12). It can be seen that the rate of nitrate removal follows the same trend as the specific growth rate in that the SGW denitrification rate is faster than 199-H4-4, which is faster than 199-D5-15. Dashed lines are used where sufficient data were not obtained to accurately determine the definite time progression of the concentrations and are based on normally observed behavior.

4.1.2.2 Carbon Limitations. The nitrate concentration performance level is 45 mg NO₃/L. Therefore, one operation scenario for a full-scale biological reactor may be to operate under carbon-limited conditions. Tests were run to determine if carbon limitations would affect the rate of denitrification. Figures 4.13 and 4.14 show the time dependence of the nitrate, nitrite, and acetate concentration for different stoichiometric acetate-to-nitrate ratios. Carbon ratio data are found in Tables A.12, A.9, and A.13 (Appendix A).

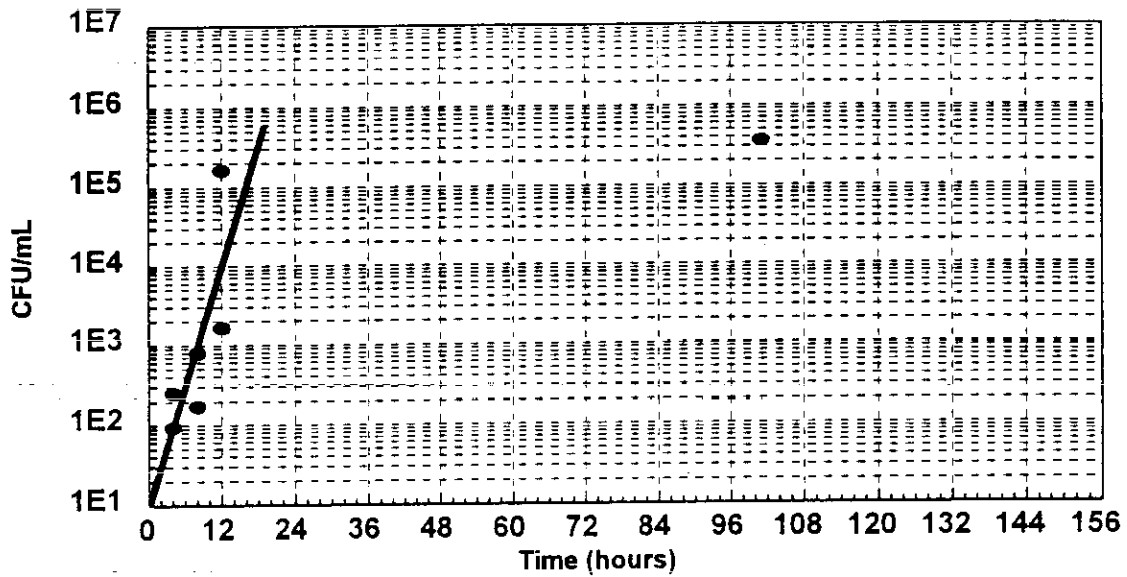


Figure 4.3. Cellular Growth Rate in High Phosphate SGW. Raw Data are Found in Table A.1

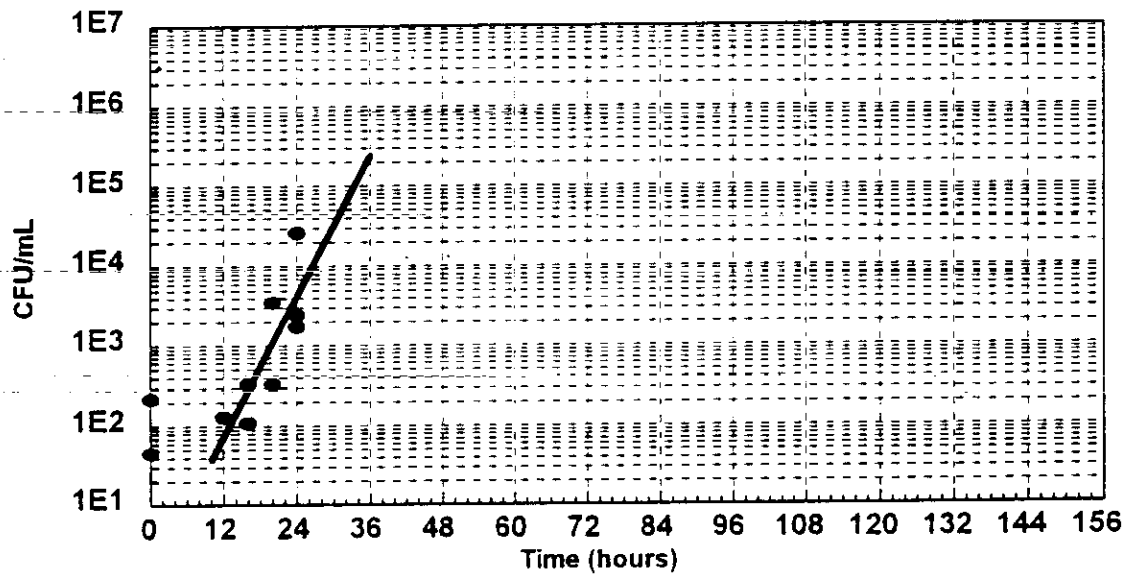


Figure 4.4. Cellular Growth Rate in SGW made according to Table 4.3. Plotted data are found in Table A.2.

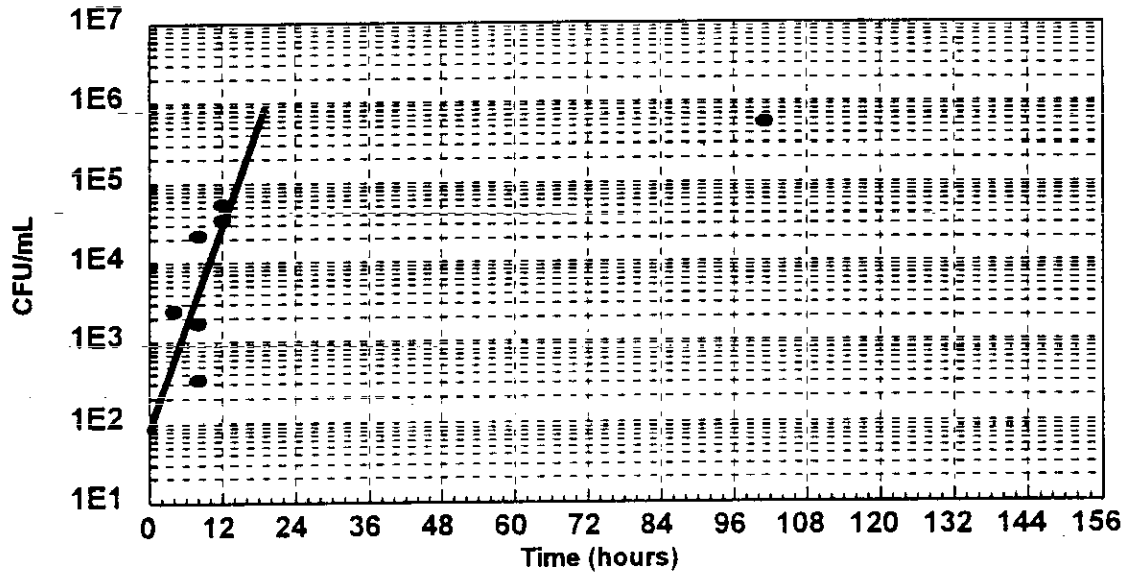


Figure 4.5. Cellular Growth Rate in Sample from Well 199-H4-4. Phosphate was not added. Plotted data are found in Table A.3.

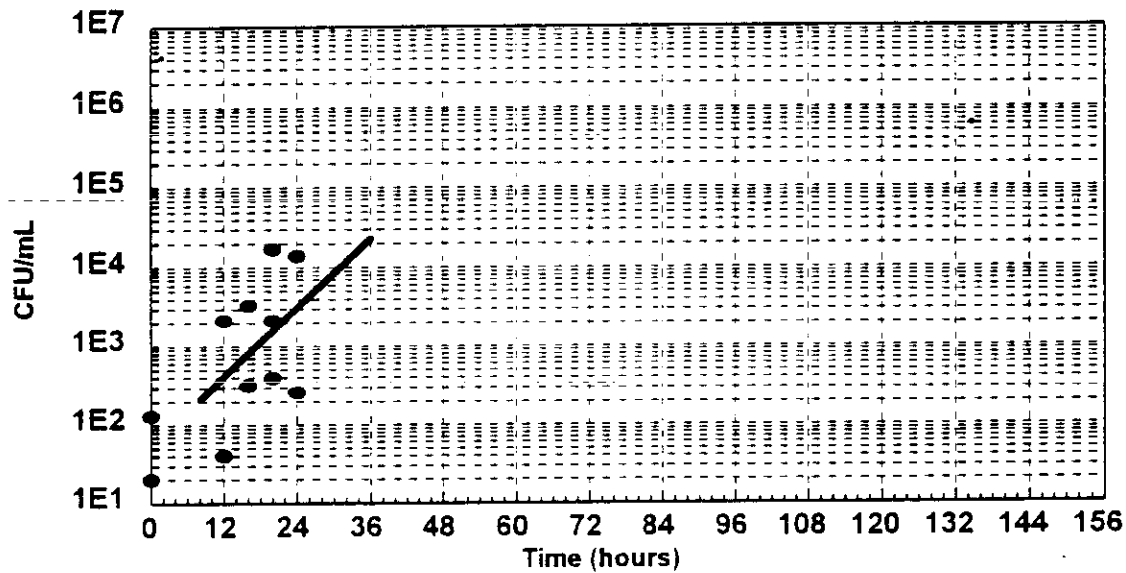


Figure 4.6. Cellular Growth Rate in Sample from Well 199-H4-4. Phosphate was added. Plotted data are found in Table A.4.

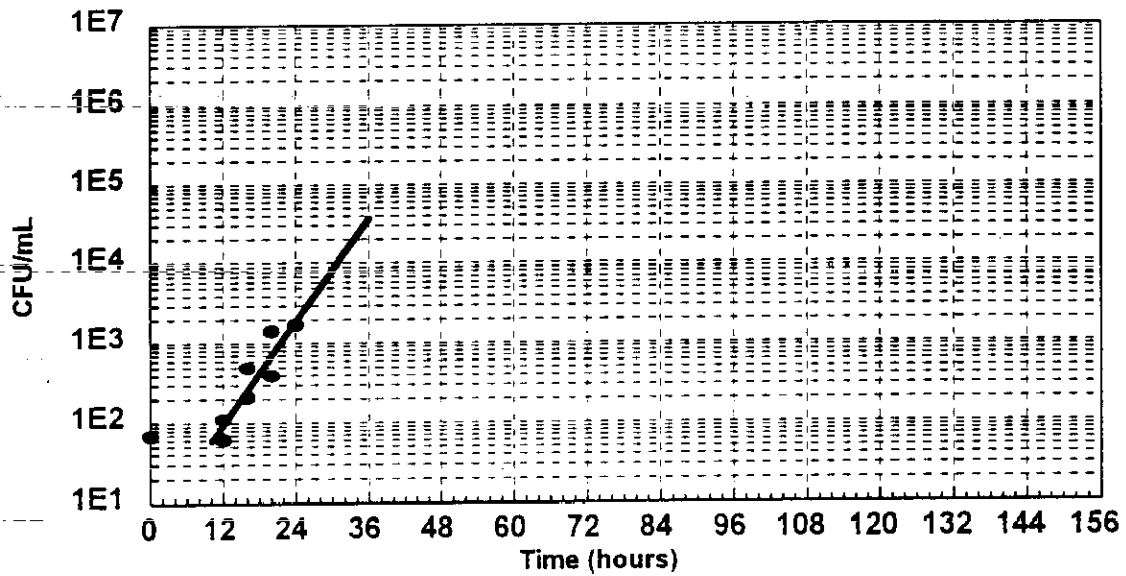


Figure 4.7. Cellular Growth Rate in Sample from Well 199-D5-15. Data are found in Table A.6.

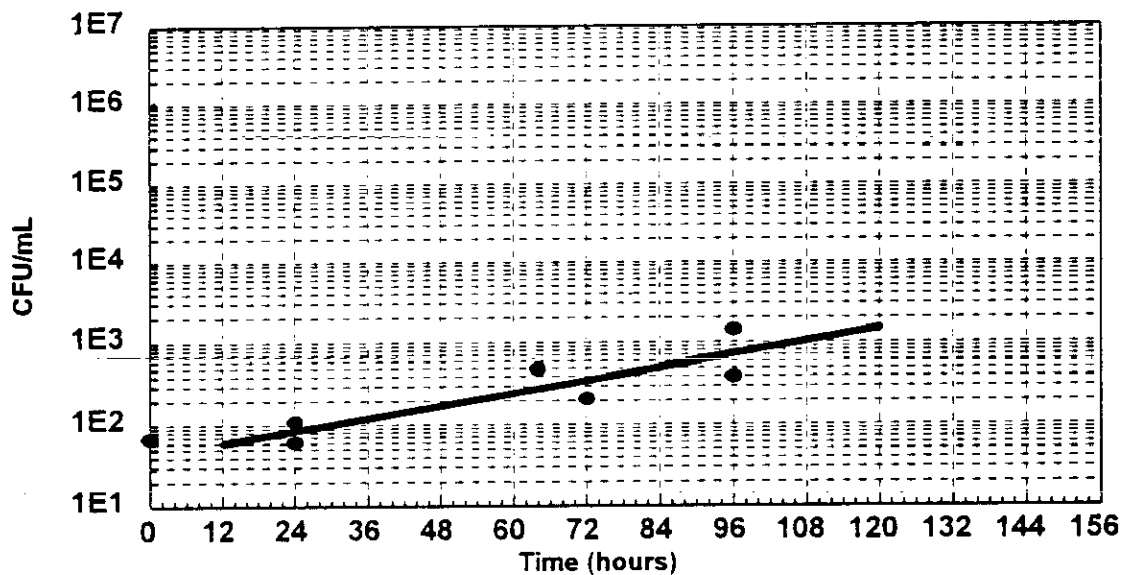


Figure 4.8. Cellular Growth Rate in Sample from Well 199-D5-15. Data are Found in Table A.7.

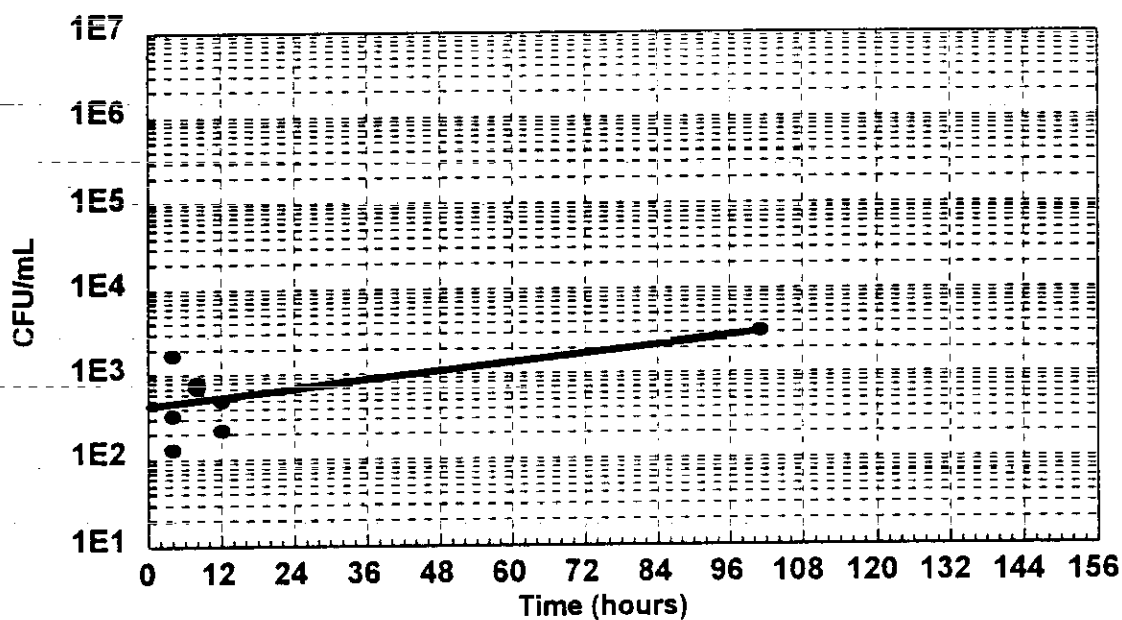


Figure 4.9. Slower growth was observed in groundwater from well 199-D5-15. Data are Found in Table A.5.

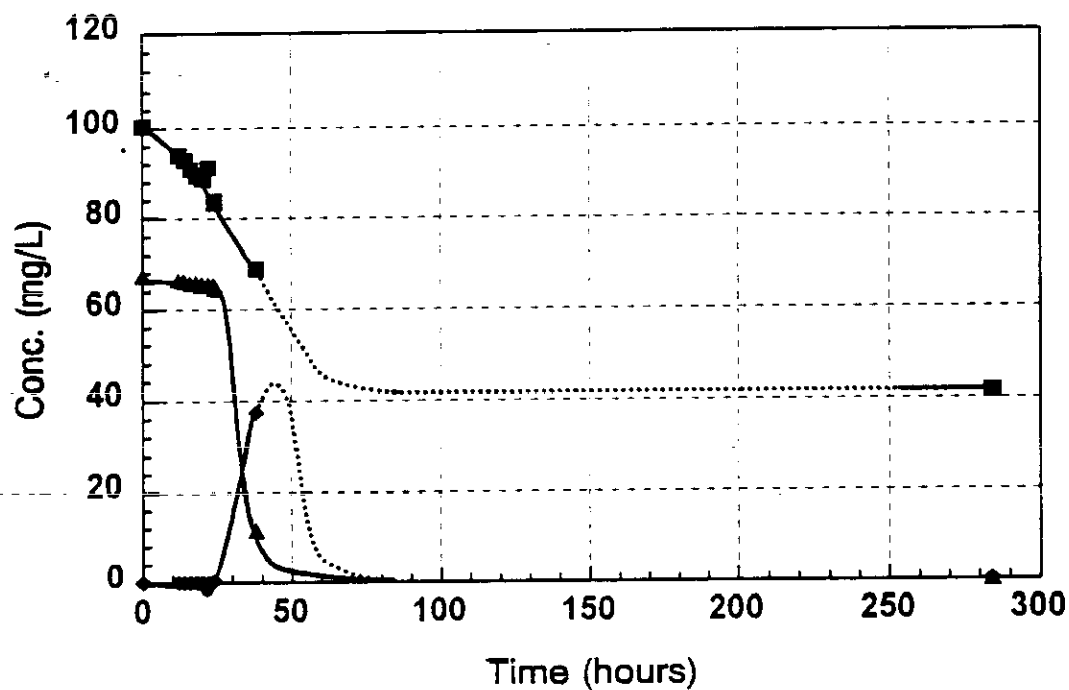


Figure 4.10. Typical Time Progression of Nitrate, Nitrite, and Acetate Concentrations in SGW (Data Table A.2). Legend: Δ - Nitrate; \diamond - Nitrite; \blacksquare - Acetate.

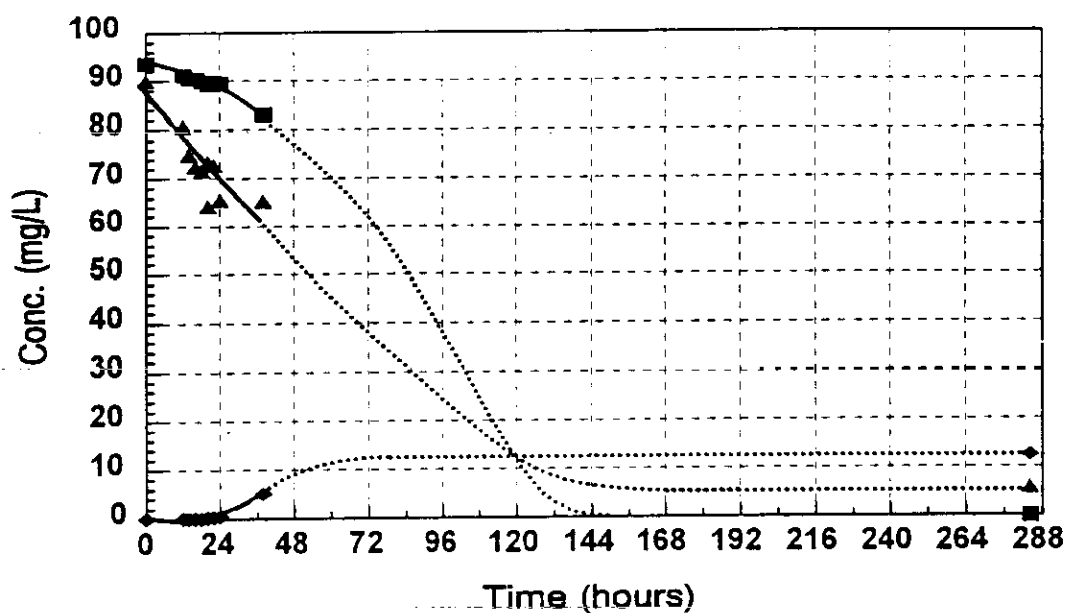


Figure 4.11. Time Progression of Nitrate, Nitrite, and Acetate Concentrations in Sample from Well 199-H4-4 (Data Table A.4). Legend: \blacktriangle - Nitrate; \blacklozenge - Nitrite; \blacksquare - Acetate.

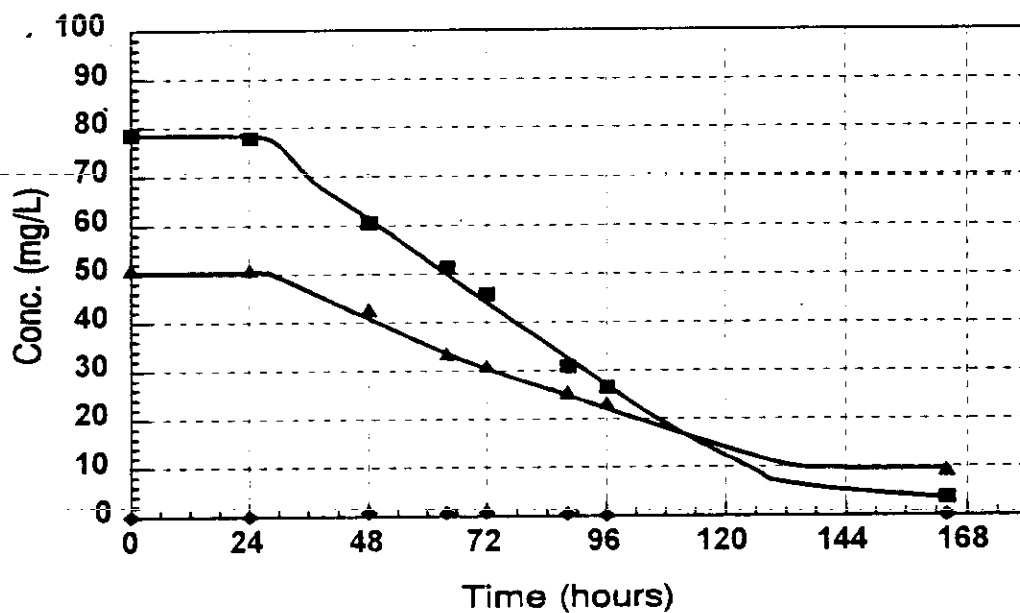


Figure 4.12. Time Progression of Nitrate, Nitrite, and Acetate Concentrations in Sample from Well 199-D5-15 (Data Table A.7). Legend: \blacktriangle - Nitrate; \blacklozenge - Nitrite; \blacksquare - Acetate.

It can be seen in Figure 4.13 that the nitrate concentration is reduced approximately two-thirds (from 57 mg/L to 20 mg/L) during the course of the test. This was to be expected since only two-thirds of the stoichiometrically required amount of acetate was added. Similarly, when a 1:1 stoichiometric ratio of acetate to nitrate was added to the shake flask, as shown in Figure 4.14, both the acetate and nitrate were depleted at the same time. In Figure 4.15, a 3:2 stoichiometric ratio of acetate to nitrate was used. This acetate to nitrate ratio consumes all the nitrate while leaving excess acetate. It is not known why a nitrite residual occurred in this test. Since this test was run with groundwater obtained from a different sampling period, the different initial nitrate concentration is likely because of variations in groundwater sample nitrate concentrations. These tests confirm Equation 6 in Section 3.2.2, provided enough acetate is present to denitrify the solution. In the pilot- and full-scale system, just enough carbon source will need to be added to reduce the nitrate and nitrite concentrations below the performance level. This will reduce chemical operating costs and ensure that excess organic carbon is not disposed with the process effluent.

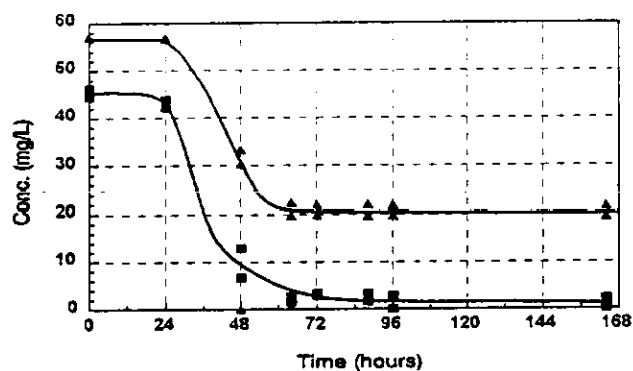


Figure 4.13. 2/3 Stoichiometric Ratio Acetate Limits the Extent of Denitrification in Composite Groundwater (Data Table A.14). Legend: ▲ - Nitrate; ■ - Acetate. Nitrite was not detected.

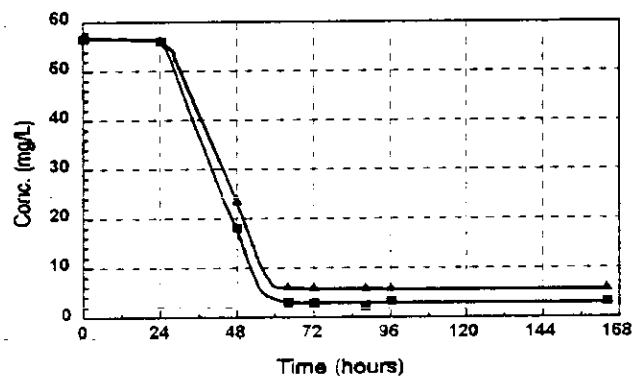


Figure 4.14. 1:1 Stoichiometric Ratio Acetate in Composite Groundwater (Data Table A.15). Legend: ▲ - Nitrate; ■ - Acetate. Nitrite was at Detection Limit of 1 mg/L.

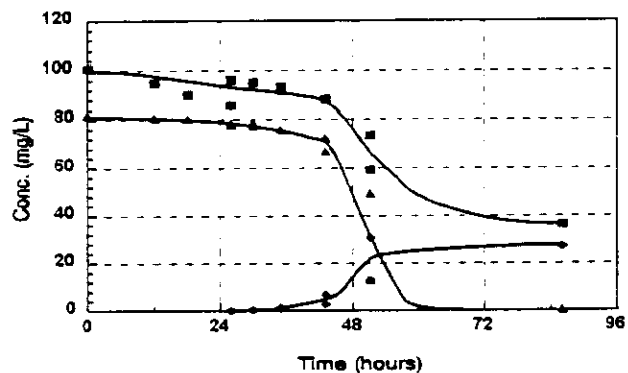


Figure 4.15. 3/2 Stoichiometric Ratio with Composite Groundwater has Excess Acetate after All Nitrate has been Removed (Data Table A.9). Legend: ▲ - Nitrate; ◆ - Nitrite; ■ - Acetate.

4.1.2.3 pH Dependence. Figure 4.16 shows the effects of different pH values on the time progression of the nitrate concentrations. It can be seen that pH 7 removed nitrate most rapidly, followed by pH 8 and 6. Data for pH dependence are found in Tables A.8 to A.11. Although the results are not included on Figure 4.16, one flask at pH 6 did not show any denitrification activity, indicating that pH 6 is on the limit for biological activity. This result follows a similar trend observed in the literature and is shown in Figure 4.17. The large volume denitrification test and the final confirmation tests were run at the natural raw water pH to give a more representative picture of the actual conditions, under a regime of minimal chemical addition. At the pilot-scale, provisions should be made in case some pH adjustment is necessary.

During the treatability tests, varying amounts of nitrite were produced. Although the detection limit is only 1 mg/L, in many tests nitrite was not detected. However, at pH 6, nitrite concentrations up to 59 mg/L were observed. The experiment was stopped after the nitrate concentration was reduced to less than 1 mg/L. At this time, 3/4 of the nitrite produced still remained in solution, with only 1/4 of the nitrite degraded. Since the maximum EPA allowable nitrite concentration is 10 mg NO_2/L (3.3 mg $\text{NO}_2\text{-N}/\text{L}$) (US EPA 1971), at the pilot-scale, both nitrate and nitrite concentrations will have to be monitored carefully to insure complete degradation. This accumulation of nitrite at low pH should not be a problem since the pilot-scale denitrification process will not be operated at pH 6 because of the low nitrate reduction rates. Nitrite degradation at pH 7 and 8 was rapid.

In addition to the fact that initial pH affects the denitrification rate, it was desirable to know the effects that denitrification had on the final pH. The process of denitrification removes hydrogen ions (H^+) from solution. Therefore, the pH of a reactor will tend to go up as a result of denitrification. The actual amount of increase in pH is determined by two factors: 1) alkalinity, and 2) carbonic acid from CO_2 production. The alkalinity of the 100 Area groundwater is approximately 100 mg/L as CaCO_3 , giving an indication of the good buffering capacity of the groundwater. The rate of H^+ removal depends on the denitrification rate, while the carbonic acid production depends both on the amount of denitrification and the amount of aerobic degradation present in the reactor. Because of the relatively low nitrate concentrations present in the 100 Area treatability tests, the pH remained relatively stable, indicating a balance between carbonic acid formation, H^+ removal, and buffer capacity. This is illustrated in Figure 4.18.

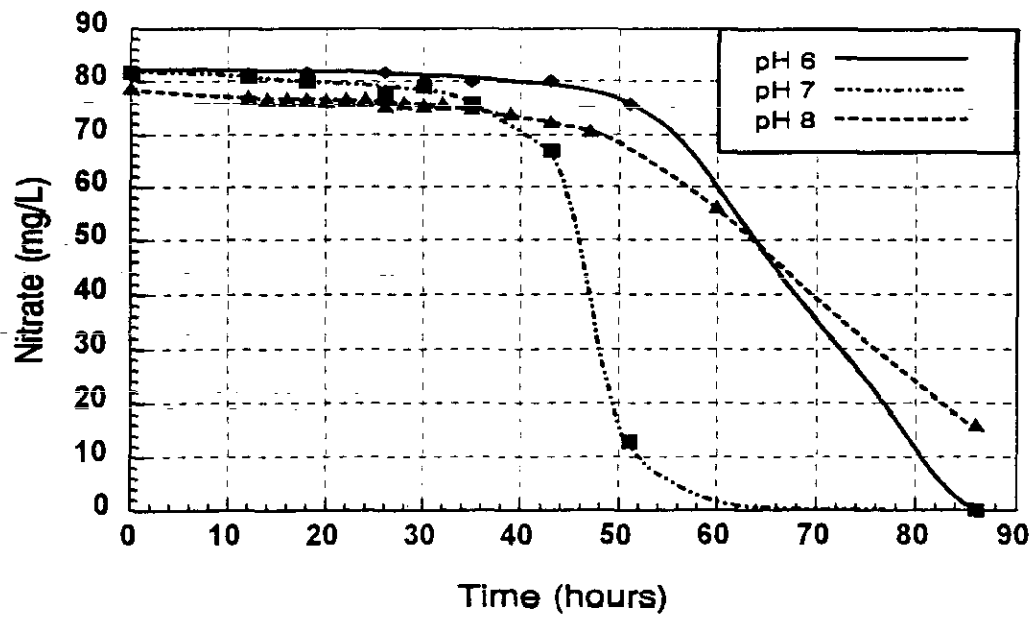


Figure 4.16. Time Progression of Nitrate Concentration in Composite Groundwater at pH 6, pH 7, pH 8.

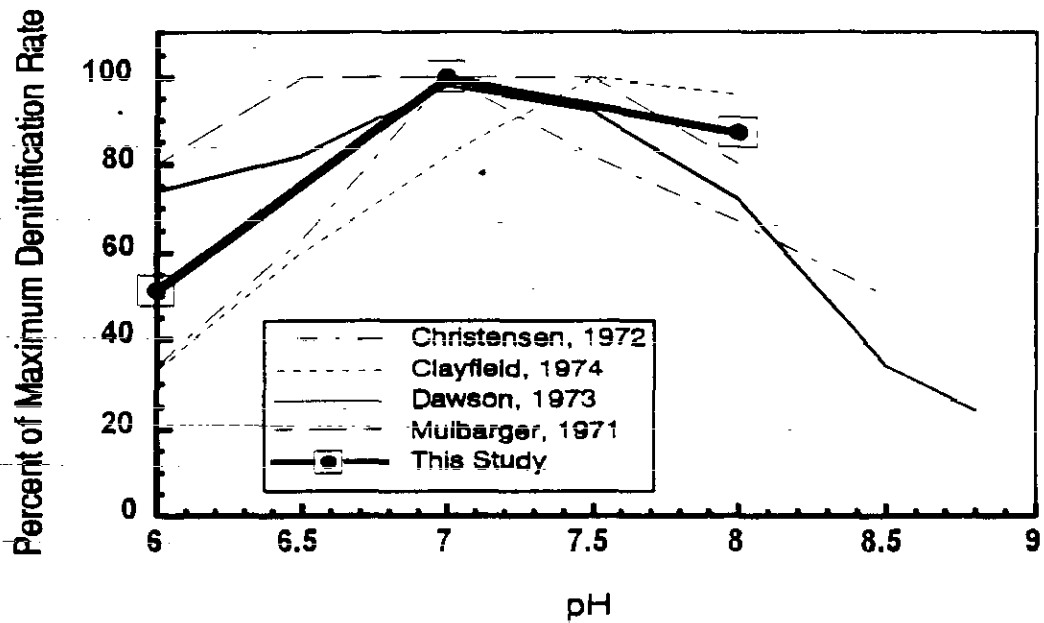


Figure 4.17. Observed Dependencies on pH plotted with data from US EPA (1975). Data are from Table 4.1.

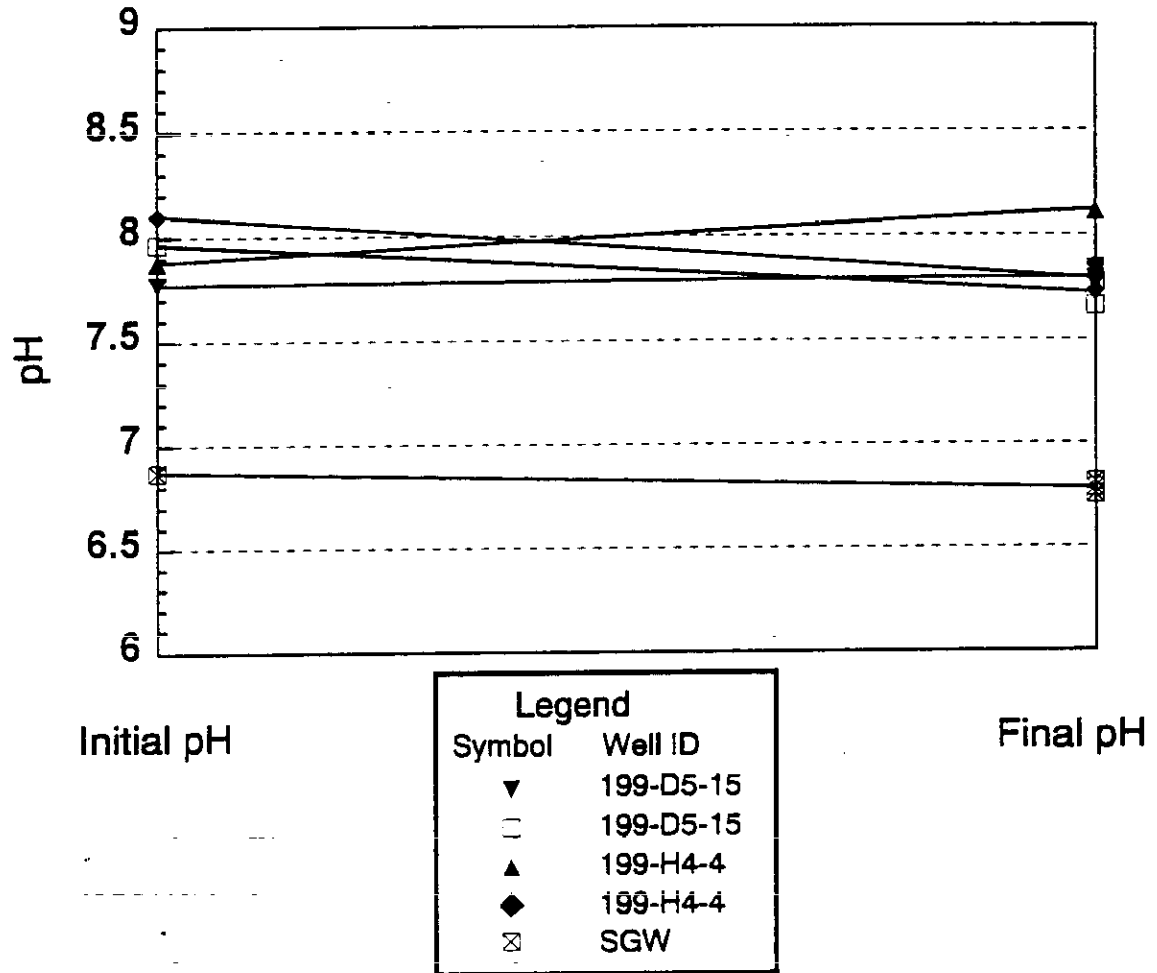


Figure 4.18. Initial and Final pH During Denitrification Tests. The minimum test duration shown was 101 h.

4.1.2.4 Temperature Dependence. Figure 4.19 shows the effects of temperature on the time progression of the nitrate concentration. This is a commonly observed trend for microbial reaction rate kinetics, and follows closely the trends given in the EPA (1975) Manual for Nitrogen Control. The Hanford consortia appears to be slightly less sensitive to temperature than the results published by Dawson and Murphy (1972). A value of the activation energy, E_a , was obtained from modeling analysis of the treatability test results. It is -12,000, rather than -16,800 (cal g-mol^{-1}), although no statistical evaluation was performed.

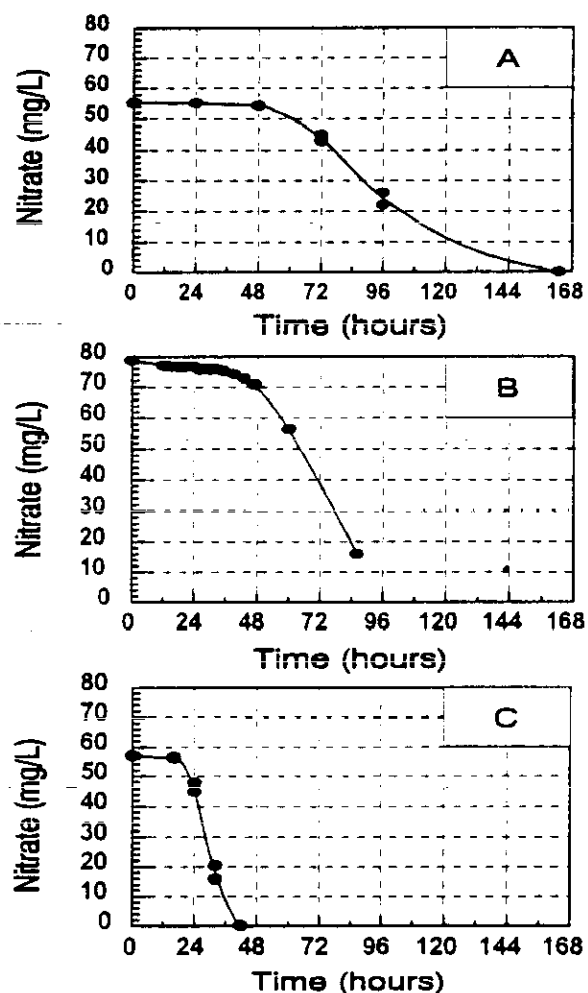


Figure 4.19. Comparison of Nitrate Concentration Reduction in Composite Groundwater at (A) 15°C, (B) 25°C, and (C) 35°C. Data from Tables A.12, A.9, and A.13, Respectively.

4.1.2.5 Acetate and Methanol Comparison. Acetate and methanol were compared for use as a carbon source for running the treatability tests. Acetate was chosen as a test compound because it is non-flammable, easy to measure, and gives good denitrification rates. Methanol is the industry standard because of cost-benefit ratio at very large scales. Methanol, however, is flammable with a flashpoint of 52°F (13.9°C), and gives a slightly slower rate of denitrification (Figure 4.20). The flashpoint of acetic acid is listed on the material safety data sheets (MSDS) as 103°F (39°C).

The February 22, 1993, Chemical Marketing Reporter indicates that the price of methanol was \$0.154/Kg methanol, and acetate was \$0.727/Kg acetic acid. Acetate is the deprotonized form of acetic acid. Calculations based on the stoichiometric ratio of each carbon source indicates that the cost for nitrate removal with methanol would be \$0.086/Kg nitrate, whereas the cost for acetate would be \$0.599/Kg nitrate. The cost ratio of these two carbon sources is 6.96, indicating that acetate would be nearly seven times more expensive in raw chemical costs as compared to methanol. Because of the relatively small amount of nitrate present in the groundwater, however, this cost ratio may be somewhat misleading. Estimated raw chemical costs were calculated for a nitrate removal of 40 mg NO₃/L at four process flow rates (Table 4.5).

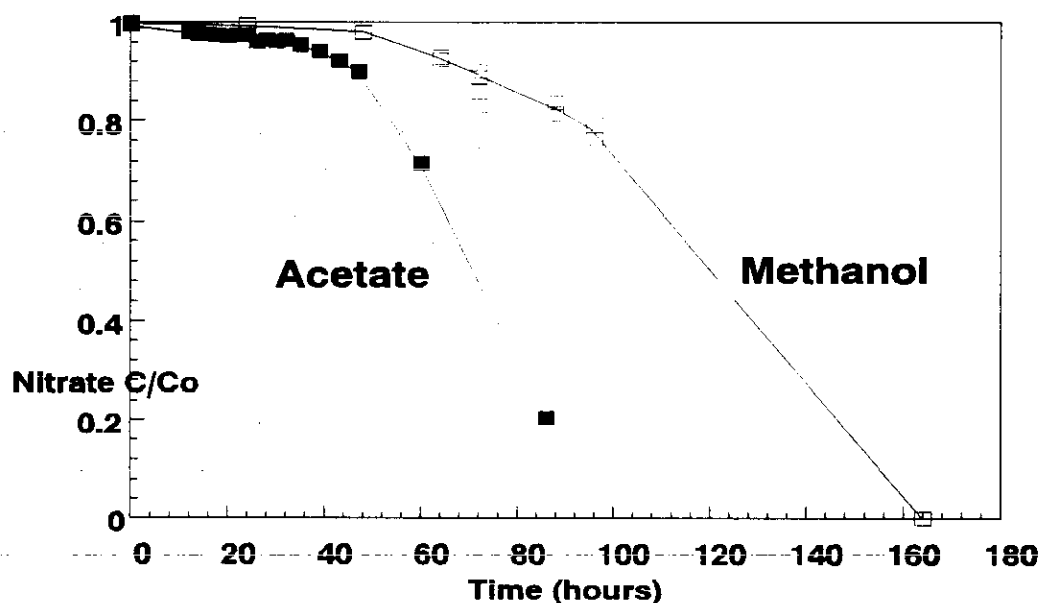


Figure 4.20. Nitrate Removal over Time with Acetate and Methanol in Composite Groundwater. Data found in Table A.9 and A.17, Respectively.

Table 4.5. Estimated Annual Raw Chemical Costs for Alternative Carbon Sources (Acetate and Methanol) with Process Flow Rate.

<u>Flow rate (gpm)</u>	<u>Cost for acetate</u>	<u>Cost for methanol</u>
1000	47,600	6,830
100	4,760	683
10	476	68
1	48	7

Although Table 4.5 was not adjusted for volume discounts and handling costs, it can be seen that at a very large scale (1,000 gpm) significant savings could be achieved using methanol, but at smaller scales the savings become less with regard to the costs for the rest of the project and the required significant increase in safety considerations for the use of methanol. To obtain more information on the Hanford consortia's response to methanol, the two final tests (large volume denitrification and final confirmation tests) were run using methanol as the carbon source.

4.1.2.6 Large Volume Denitrification for Chemical Precipitation. This test was run at 20°C and the natural pH of 7.8, and the denitrified water was transferred to WHC for further testing of metals removal processes. Methanol was used as the carbon source because of the potential for significant savings in operating costs at a very large scale. The pH was monitored and after a few days was found to vary between 7.0 and 7.1. This drop in pH is probably the result of carbon dioxide solubility. This explanation is further supported by the fact that subsequent sparging of the solution with helium raised the pH to 7.9.

The large amount of methanol required to denitrify the groundwater (Figure 4.21) is likely the result of oxygen leakage into the fermentor. The stoichiometry of nitrate to methanol removal in the large volume test is much less than observed in either the methanol tests or the final confirmation tests. Pilot-scale equipment should be designed to minimize the amount of oxygen entering the system.

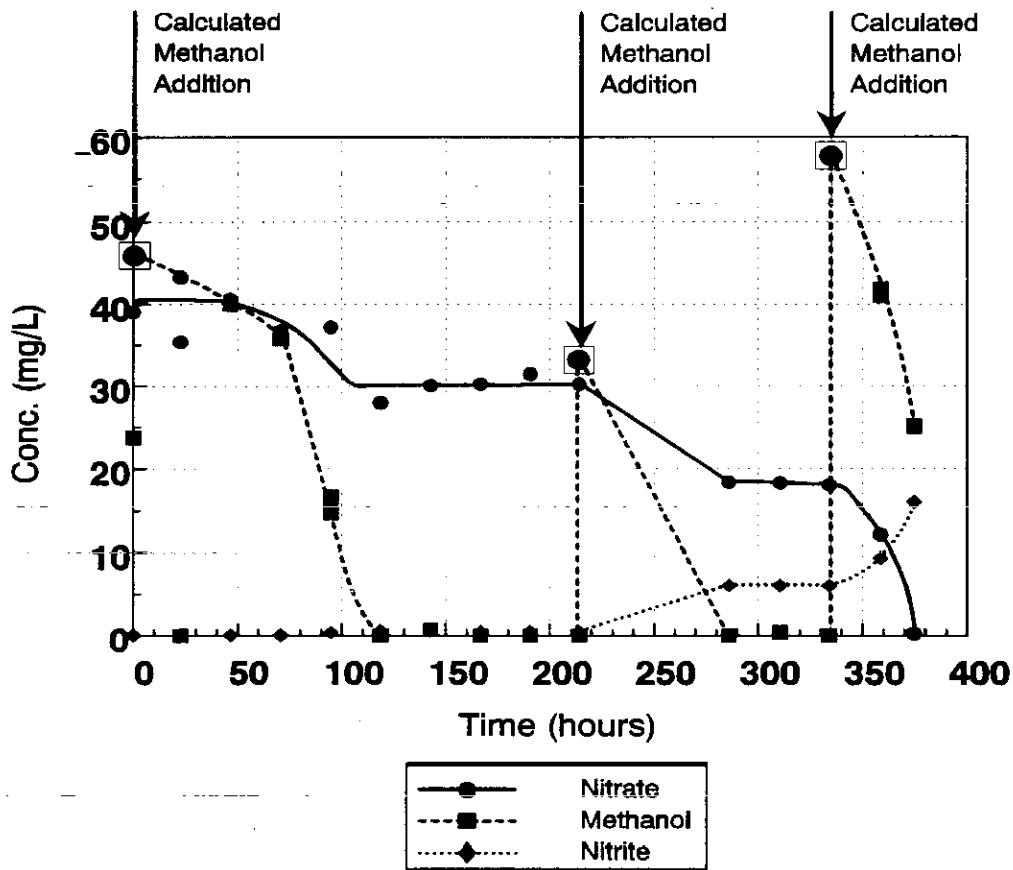


Figure 4.21. The Large Volume Denitrification Fermentor had Significant Oxygen Leaks, Causing Much More Methanol to be Required for Nitrate Removal in Composite Groundwater (Data Table A.16).

4.1.2.7 Final Confirmation Testing. In Figure 4.22, data for methanol, nitrate, and nitrite are shown for all six replicate flasks (from data Tables A.19 to A.23, Appendix A). The scatter for nitrate and nitrite removal is typical for biological tests; however, the larger scatter for the methanol data is probably representative of oxygen leaks in some flasks. The probability of an oxygen leak was increased by the frequency of sampling and the removed sample size. It can be seen in Figure 4.22 that the flasks were sampled quite frequently. It should also be noted that the sample volume required by the external lab was four times higher than what was required for our internal analyses. These tests confirm the results obtained in the earlier methanol tests and provide kinetic data to design a pilot-scale nitrate treatment unit.

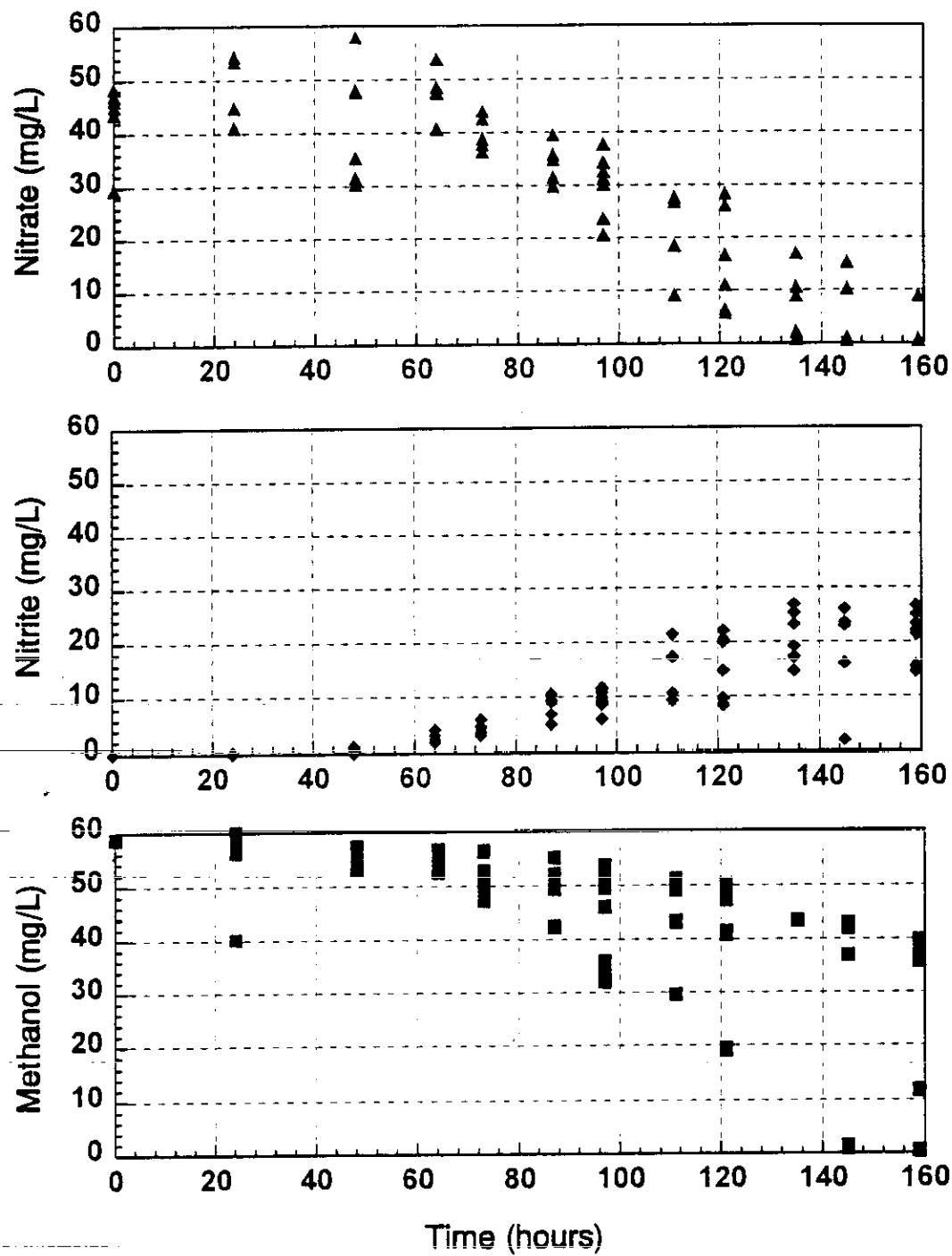


Figure 4.22. Final Confirmation Test Data on Composite Groundwater Scatter-plot for Six Replicate Flasks. Data Found in Tables A.19 to A.23.

Radionuclide removal data are given in Table B.1 (Appendix B). Gross alpha levels were reduced from an average of 7.2 pCi/L to 5.4 pCi/L, indicating a 25% reduction in gross alpha. Because of few samples, the confidence interval is large around each average. The 68% confidence interval for the value 7.2 is from 9.05 to 5.35 pCi/L. For the 5.4 value, the confidence interval is from 6.95 to 3.85 pCi/L. Therefore, the data obtained on gross alpha do not show a statistically significant removal at the 68% confidence level. Although the biological removal of gross alpha emitters from the groundwater appears promising even with the very low biomass concentrations, more measurements will need to be made at the pilot-scale to determine if the reduction is significant. Gross beta levels were only reduced an average of 2.5%, dropping from an average 31.05 to 30.25 pCi/L, indicating that very little reduction was observed. The significance of this result must also be taken cautiously since few measurements were made in the determination, and the biomass concentration was so low that it would be difficult to measure a change in the radionuclide concentrations.

The measurement of total suspended solids was made using a 0.2 micrometer filter, rather than the larger pore standard glass fiber filters, because the final biomass concentration was undetectable using the larger pore filters. Suspended solids data and qualitative observations regarding settling and filtration are given in Appendix C. Measurements using this method will give higher values for the suspended solids measurements than the methods typically used to examine wastewater. Therefore, the results given here should be viewed as the maximum biomass production from the degradation of nitrate. The average suspended solids concentration was 9.0 mg/L with a standard deviation of 3.1 mg/L. The observed biomass yield for denitrification with methanol as a carbon source is therefore $(9.0 \text{ mg TSS/L}) / (45 \text{ mg NO}_3\text{/L})$ or $0.2 \pm 0.066 \text{ mg TSS/mg NO}_3$. Raw suspended solids data are given in Table C.1.

4.1.3 Comparison to Test Objectives

Specific test objectives are listed below:

1. Determine if inhibitory compounds are present - Because the 100 Area groundwater may contain compounds that inhibit microbial denitrification, tests were run to determine if the rate and extent of denitrification in the groundwater was comparable to the rates commonly expected. This objective was accomplished by comparing denitrification and growth rates in 100-HR-3 groundwater to rates in a SGW under identical conditions. While the growth rates in raw groundwater were not as high as those observed in the SGW, denitrification rates were sufficient to reduce nitrate concentrations to below the performance levels.
2. Determine the extent to which carbon limitations affect denitrification - This was done to ensure that nitrate was indeed the rate limiting nutrient and to determine the effects of carbon limitations on denitrification rates. Since the MCL for nitrate is 45 mg/L, a pilot-scale system may be operated in a carbon limited manner and still remove enough nitrate to effectively remediate the effluent water, although careful measurement and control of nitrite will be required. The extent of denitrification behaved as expected based on the reaction stoichiometry, and the rates were not affected by having a carbon-limited, rather than a nitrate-limited, environment.
3. Determine denitrification rates at pH values 6, 7, and 8 - The biochemical reactions for biodenitrification results in an increase in the solution pH. Depending on the buffering capacity of the groundwater, this increase may be large or small and may affect denitrification rates. In addition, information on the effect of pH on denitrification rates may play a significant role in integrating chemical and biological treatment at this site since pH control plays an important role in chemical precipitation. Initial measurements of groundwater pH were between 7.6 and 8.0. An effect of pH on the maximum growth rate was observed. At pH 6, the specific growth rates were approximately one-half that of pH 7. In unbuffered groundwater, the change in pH in these tests was very small because of the low nitrate concentrations. At this time it cannot be determined if pH adjustment would be more or less cost effective than potential increased equipment sizing.
4. Determine the effect of temperature on the rate of denitrification - Even with a relatively stable groundwater temperature, an ex-situ process at the Hanford Site may expect certain temperature fluctuations throughout the year. This objective, specifically, was to determine denitrification rates at 15°C, 25°C, and 35°C. Generic rate expressions that account for the effect of temperature on denitrification rates exist, but the constants should be verified under site-specific conditions. The groundwater temperature in the 100 Area was typically in the range 17 to 20°C. The growth rate of the Hanford consortia appears to depend on temperature slightly less than limited literature data suggest. A value for the activation energy in the Arrhenius Equation, E_a , of -16,800 (cal/gmole) given by Dawson and Murphy (1972), is slightly lower than the value near -12,000 obtained from this data.
5. Determine carbon source and dosage - The role of the carbon source is important in determining denitrification and biomass production rates. The carbon sources that were compared are acetate and methanol. Methanol is an industry standard because of its cost, but acetate gives faster denitrification rates. Dosage was determined by analyzing observed yield values after removing nitrate and producing biomass. The desirable carbon source would be inexpensive and support a high denitrification rate while producing a small amount of biomass.

Initial dosage was determined from Equation 5 or 6. These tests gave data to predict the amount of carbon source required to remove a specific amount of nitrate from groundwater. Both carbon sources gave good denitrification rates, although acetate gives faster denitrification. Cost and safety issues will still need to be determined before the pilot-scale treatment process.

Final confirmation tests and their results are listed below:

1. Confirm that performance levels could be met - A final set of integrated batch tests were performed to evaluate the site-specific reaction rate kinetics and confirm that denitrification could reach the desired performance levels of 45 mg/L in 100 Area groundwater. These tests showed that bionitrification could reduce nitrate concentrations far below the 45 mg/L.
2. Determine the amount of chromium and radionuclide adsorption to biomass - Although some information is available on the extent of chromium uptake by the Hanford denitrifying consortia, the information on the extent of radionuclide adsorption is limited. Radionuclide removal in the form of gross alpha and beta gave mixed results. A removal of 25% of gross alpha appears promising, though 2.5% for gross beta is not. The statistical significance of the removal for gross alpha is low due to the relatively few samples and very low biomass concentrations. The measured reduction of 15 $\mu\text{g/L}$ (1.5%) for chromium was from 990 ± 80 to $975 \pm 80 \mu\text{g/L}$. In both the radionuclide and chromium data, contaminant reductions are not statistically significant.
3. Recommend bioreactor types for pilot-scale tests - Bioreactor types that should be evaluated at the pilot-scale are recommended based on denitrification rates observed in these tests. The recommendation does not include information about costs. For simplicity to build and operate, and because of the relatively low amounts of nitrate to be removed, either a fluidized bed reactor or a packed bed reactor is recommended (see Section 4.1.4 for details).

4.1.4 Recommended Bionitrification Reactor Designs

Two basic types of continuous biological reactors can be used to remove nitrate from a groundwater stream: 1) suspended growth and 2) fixed film. In a suspended-growth reactor, nearly all microorganisms are free-floating in the liquid phase. This reactor type is more sensitive to both chemical and hydraulic "shocks" since the microbes can be completely washed out of the system. Most suspended-growth systems are operated in the form of an activated sludge process, whereby biomass from a downstream clarifier is reintroduced into the reactor to boost the biomass concentrations. Suspended-growth reactors do not require periodic backwashing and are easy to operate if relatively stable conditions are expected, and viable biomass can be readily separated for recycling. Suspended-growth systems have a lower biomass concentration and therefore typically require a larger hydraulic retention time than fixed-film reactors.

A fixed-film system is a biological reactor that has biomass attached to some type of solid support media. Three typical fixed-film configurations include 1) deep-bed filters, 2) rotating biological contactors (RBC), and 3) fluidized bed reactors (FBR). Each fixed-film reactor configuration has certain advantages and disadvantages.

Deep-bed filters are columns packed with an inert packing material. Microbes attach to the material while at the same time nitrate containing water is passed through the packed bed. The advantages are that few moving parts are required and efficient nitrate removal can be achieved. Disadvantages are that the unit requires periodic backwashing to maintain open flow channels for the water to pass through and to prevent plugging of the column. Biomass that detaches from the solid media can plug the flow channels causing "short-circuiting" or channeling of the process stream. This channeling causes the mean liquid residence time of the reactor to decrease, and contaminant breakthrough can occur. For continuous operation, the requirement for periodic backwashing can mean that the reactor must be taken off-line. In this case, a second deep-bed filter is required to maintain continuous operation.

Rotating biological contactors are reactors composed of liquid holding tanks with shaft-mounted rotating disks for microbial attachment. The rotation of the disk mixes the liquid for increased mass transfer to the attached film. The RBC's do not suffer from problems of channeling, but do require some type of biofilm removal. This is usually achieved on a continuous basis with some type of scraper arrangement to physically remove the biofilm after it has reached a predetermined thickness. Fluidized bed reactors have the same advantages as a deep bed filter without the problems associated with channeling and plugging. This is because the packing material is "fluidized" or suspended by the force of water moving upwards through the reactor. An FBR has good mixing characteristics and has the fastest denitrification rate per unit reactor volume. Disadvantages include a more technical start-up period to achieve good fluidization and the added equipment required to separate entrained solids from attached biomass.

Guidance from the 100-HR-3 Groundwater Treatability Test Plan (DOE/RL-92-73) recommends a pilot-scale process flow rate of 1 to 5 gpm, so only continuous flow biological reactors are addressed here. A hybrid reactor, called a sequencing batch reactor (SBR) could be used at the pilot scale and should be addressed. The SBR is filled with contaminated liquid, allowed to react for a set period of time, and then emptied after the contaminant concentration has been reduced to an

acceptable level. This is the SBR process cycle. Typically, SBR's are used for high concentrations of slowly reacting species. This allows more control over the process. A disadvantage of this is that fast process cycling requires more attention than comparable continuous processes. Because of this, SBR's are less commonly used for low concentrations of fast-reacting species, such as nitrate near the drinking water standard. A typical SBR process cycle is on the order of 12 to 48 h. The cycle includes the following steps: fill with liquid, react to degrade contaminant, settle biomass, decant clean effluent. Then the cycle starts again. For a process flow rate of the recommended 1 to 5 gpm, a 12-h cycle time would require two 720- to 3,600-gal reactors. If the pilot- or full-scale chromium removal process were to be operated as a batch process, then an SBR may be beneficial.

In summary, based on the relatively low nitrate concentrations found in the 100 Area operable unit, a fixed-film reactor system is recommended for further pilot-scale studies. For simplicity, a deep-bed fixed film reactor with an open (very porous) packing is recommended.

4.2 QUALITY ASSURANCE/QUALITY CONTROL

The goal of this project is to provide quality data to aid in designing a pilot-scale denitrification and chromium removal facility. Every effort was made to meet both the spirit and the letter of the existing QA requirements. The guiding document for this effort is the Quality Assurance Project Plan (QAPjP) given in Appendix B of the "100 Area Groundwater Bench-Scale Treatability Study Procedures" (Peyton and Martin 1993).

The data quality objectives (DQO) found in Table 4.6 were formulated using the definitions found in Section 4.2.1.

4.2.1 Data Quality Objectives Definitions

For measurements where standard reference materials (SRM) were used, percent recovery was calculated.

$$\%R = 100 \times \frac{S}{C_{sa}} \quad (14)$$

where

%R = percent recovery

S = measured concentration in aliquot

C_{sa} = actual concentration of reference material

For this project, measures of analytical precision were determined by analyzing laboratory duplicates. Laboratory duplicates were prepared by homogenizing and splitting a sample in the laboratory and then carrying the subsamples through the entire analytical process. Precision can be expressed in terms of the relative percent difference (RPD).

$$RPD = \frac{(C_1 - C_2)}{[(C_1 + C_2) / 2]} \times 100 \quad (15)$$

where

RPD = relative percent difference

C₁ = larger of the two observed values

C₂ = smaller of the two observed values

A measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions is defined as the completeness of the data.

$$\%C = 100 \times \frac{V}{n} \quad (16)$$

where

V = Number of Valid Data Points Acquired

n = Total Number of Data Points

The detection limit is the minimum concentration of a substance that could be measured and reported. Method Detection Limit (MDL) is the minimum concentration of a substance that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero. The detection limits were lower than the performance levels stated in the 100-HR-3 Groundwater Treatability Test Plan, Table 1.2.

The MDL is defined as follows:

$$MDL = t_{(n-1, 1-\alpha=0.99)} = S \quad (17)$$

where

MDL	= method detection limit
S	= standard deviation of the replicate analyses
$t_{(n-1, 1-\alpha=0.99)}$	= Students' t-value appropriate to a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom

4.2.2 Observed Data Quality

The data quality objectives found in Table 4.6 were designed so that gross errors in data quality would fall outside the range for relative percent difference and percent recovery. Actual data were of much higher accuracy and precision.

The most important parameter to this study, nitrate, had a relative percent difference of approximately 5 to 10% at concentrations above 20 mg/L. The percent recovery (%R) for an NIST standard of 10 mg/L were in the range of 90-110%. A comparison of nitrate and nitrite concentrations measured in our lab and at the PNL 325 lab is found in Table B.2. Percent completion is greater than 100% since many more samples were analyzed than had been originally planned for.

Table 4.6. Data quality objectives for samples. References are listed at the bottom.

Analyte or parameter (measurement method)	EPA level	Analytical method	Detect. limit	Units of measure	RPD (%)	%R	Completion (%)
Temperature (Thermometric)	III	Method 170.1 Ref. 1	NA	°C	≤ 20	NA	90
pH (Electrometric)	III	Method 9040 Ref. 2	NA	pH units	≤ 20	NA	90
Methanol (gas Chromatography)	III	Method in Test Procedure Appen. A	NA	mg/L	≤ 40	50-150	75
Acetate (Ion Chromatography)	III	SOP # 93-BR6-0001	1	mg/L	≤ 40	50-150	75
Nitrate (Ion Chromatography)	III	SOP # 93-BR6-0001	1	mg/L	≤ 40	50-150	75
Nitrite (Ion Chromatography)	III	SOP # 93-BR6-0001	1	mg/L	≤ 40	50-150	75

Table 4.6. (cont.). Data quality objectives for samples.

Analyte or parameter (measurement method)	EPA level	Analytical method	Detect. limit	Units of measure	RPD (%)	%R	Completion (%)
Total Suspended Solids	III	Method 2540 Ref. 3	NA	mg/L	≤ 40	NA	75
Total Volatile Solids	III	Method 2540 Ref. 3	NA	mg/L	≤ 40	NA	75
Gross Alpha	III	PNL-ALO-460 PNL-ALO-461	10	pCi/L	≤ 40	50- 150	75
Gross Beta	III	PNL-ALO-462 PNL-ALO-463	30	pCi/L	≤ 40	50- 150	75
Bacterial Numbers (MPN)	III	Method 47-3 Ref. 5 modified for Durham tube confirmation.	1000	Bacterial Number	10-1000	NA	75
Chromium (VI) (Colorometric)	III	PNL-ALO-227	100	μg/L	≤ 40	50- 150%	75

Table 4.6. (cont.). Data quality objectives for samples.

Analyte or parameter (measurement method)	EPA level	Analytical method	Detect. limit	Units of measure	RPD (%)	%R	Completion (%)
Chromium, Total (Atomic Absorption)	III	PNL-ALO-211	50	µg/L	≤ 40	50-150%	75

1- U.S. Environmental Protection Agency. Methods for the Chemical Analysis of Water and Wastes. EPA-600/4-79-020. March 1983.

2- U.S. Environmental Protection Agency. Test Methods for Evaluating Solid Waste. Third Edition. SW-846, 1986.

3- Standard Methods for the Examination of Water and Wastewater. LS Clesceri, AE Greenberg, and RR Trussel (Eds.), 17th Edition, 1989.

4- Found in PNL-MA-567 Analytical Chemistry Laboratory (ACL) Procedure Compendium Vol. III and Vol. V.

5- Methods of Soil Analysis, Part 2 - Chemical and Microbiological Properties, Second Edition, A.L. Page, R.H Miller, and D.R. Keeney (Eds.), American Society of Agronomy, Inc., Madison, Wisconsin, 1982.

NA - Not Applicable

4.3 KEY CONTACTS

<p>Brent M. Peyton (MSIN P7-41) Pacific Northwest Laboratories Battelle Boulevard Richland, WA 99352 PH (509) 376-0537 FAX (509) 376-1867</p>	<p>Richard L. Biggerstaff (MSIN H6-02) Westinghouse Hanford Company 740 Stevens Drive Richland, WA 99352 PH (509) 376-5634 FAX (509) 376-6476</p>
<p>Dan Anderson (MSIN P7-41) Pacific Northwest Laboratories Battelle Boulevard Richland, WA 99352 PH (509) 376-9428 FAX (509) 376-1867</p>	<p>Jim Duncan (MSIN H6-05) Westinghouse Hanford Company 740 Stevens Drive Richland, WA 99352 PH (509) 372-0896 FAX (509) 376-6476</p>

5.0 REFERENCES

- Brouns, T. M., S. S. Koegler, W. O. Heath, J. K. Fredrickson, H. D. Stensel, D. L. Johnstone, and T. L. Donaldson, 1990, Development of a Biological Treatment System for Hanford Groundwater Remediation: FY 1989 Status Report, PNL-7290, Pacific Northwest Laboratory, Richland, Washington.
- Christensen, M. H. and P. Harremoës, 1972, Biological Denitrification in Wastewater Treatment, Report 2-72, Department of Sanitary Engineering, Technical University of Denmark, Denmark, Holland.
- Clayfield, G. W., 1974, "Respiration and Denitrification Studies on Laboratory and Works Activated Sludges." Water Pollution Control, 1, p 51-76.
- Dawson, R. N. and K. L. Murphy, 1972, "The Temperature Dependency of Biological Denitrification." Water Research, 6, p 71-83.
- Dawson, R. N. and K. L. Murphy, 1973, "Factors Affecting Biological Denitrification in Wastewater." in Advances in Water Pollution Research, S. H. Jenkins (ed.), Pergamon Press, Oxford, England.

- Grady, C.P.L., and H.C. Lim, 1980, Biological Wastewater Treatment, Marcel Dekker, New York.
- Koegler, S. S., T. M. Brouns, W. O. Heath, and R. J. Hicks. 1989. Biodenitrification of Hanford Groundwater and Process Effluents: FY 1988 Status Report, PNL-6917, Pacific Northwest Laboratory, Richland, Washington.
- McCarty, P. L., L. Beck, and P. St. Amant, 1969, Biological Denitrification of Wastewaters by Addition of Organic Materials, Proceedings of the 24th Industrial Waste Conference, May 6, 7, and 8. Lafayette, Indiana.
- Mulbarger, M. C., 1971, The Three Sludge System for Nitrogen and Phosphorous Removal, Presented at the 44th Annual Conference of the Water Pollution Control Federation, October, San Fransisco, California.
- Peyton, B. M. and K. R. Martin, 1993, 100 Area Groundwater Biodenitrification Bench-Scale Treatability Study Procedures, PNL-8610, Pacific Northwest Laboratory, Richland, Washington.
- Truex, M. J., D. R. Brown, and D. B. Elliott, 1992, Cost/Benefit Analysis Comparing Ex-Situ Treatment Technologies for Removing Carbon Tetrachloride from Hanford Groundwater, PNL-8334, Pacific Northwest Laboratory, Richland, Washington.
- United States Department of Energy, Richland Operations Office (DOE-RL), 1992b, "100 Area Feasibility Study Phases 1 and 2", Decisional Draft, DOE-RL-92-11, U.S. Department of Energy, Richland, Washington.
- United States Environmental Protection Agency (EPA), 1971, Water Quality Criteria Data Book, Vol.2, Inorganic Chemical Pollution of Freshwater, 18010 DPV 07/71.
- United States Environmental Protection Agency (EPA), 1975, Process Design Manual for Nitrogen Control, Office of Technology Transfer, 628.3 US84PO.
- United States Environmental Protection Agency (EPA), 1993, Manual for Nitrogen Control, Office of Technology Transfer, EPA/625/R-93/010.
- Westinghouse Hanford Company (WHC), 1988, Environmental Investigations and Site Characterization Manual, WHC-CM-7-7, Richland, Washington.
- Yamamoto, K., J. Kato, T. Yano, and H. Ohtake, 1993, "Kinetics and Modeling of Hexavalent Chromium Reduction in Enterobacter cloacae," Biotech. Bioeng., 41, p 129-133.
- 40 CFR 59569: December 24, 1974, part 248, U.S. Environmental Protection Agency, "Safe Drinking Water Act, Code of Federal Regulations."

**THIS PAGE INTENTIONALLY
LEFT BLANK**

APPENDIX A
RAW SHAKE FLASK DATA

8910-726746
9/13/22 0468

6910 776 116
94322 116

Explanation of Column Headings and Symbols used in the Tables in Appendix A.

NO₃ The standard chemical symbol for nitrate

NO₂ The standard chemical symbol for nitrite

CFU Stands for "most probable number of bacterial colony forming units."

QA Sample This column heading was used to indicate that this sample was a replicate of another sample, and could be used to calculate the quality assurance relative percent difference parameter.

--- Indicates that a sample was not taken or analyzed.

ND Indicates that the analyte was "Not Detected" or that the concentration was below the method detection limit.

0245-2246
94322-970

Table A.1. SGW Inhibition Test 1, Replicates 1 and 2. See Comment Below Regarding Phosphate Concentration of this Test.

Time (h)	NO ₃ (mg/L)	NO ₂ (mg/L)	Acetate (mg/L)	CFU (#/mL)	QA Sample	Sample ID
Replicate 1						
4	---	---	---	9.3E+02	---	54999-12-S-3
8	---	---	---	1.7E+03	---	54999-12-S-5
12	---	---	---	1.6E+04	---	54999-12-S-7
101	---	---	---	3.5E+06	---	54999-12-S-9
Replicate 2						
4	---	---	---	2.5E+03	---	54999-14-S-3
8	---	---	---	7.9E+03	---	54999-14-S-5
12	---	---	---	1.6E+06	---	54999-14-S-7
101	---	---	---	3.5E+06	---	54999-14-S-9

Comments: These data were used to make Figure 4.3, which shows CFU increases in a very high phosphate buffer concentration (13,600 mg KH₂ PO₄/L). This concentration of phosphate was reduced to allow ion chromatographic analysis of nitrate and to prevent possible calcium or magnesium phosphate precipitation. Subsequent SGW formulations were made as written in Table 4.6 using only 68 mg KH₂ PO₄/L.

Table A.2. SGW Inhibition Test 2, Replicates 1 and 2.

Time (h)	NO ₃ (mg/L)	NO ₂ (mg/L)	Acetate (mg/L)	CFU (#/mL)	QA Sample	Sample ID
Replicate 1						
0	67.4	ND	100.53	2.20E+03	---	54999-32-S-1
12	66.45	ND	94.00	1.30E+03	---	54999-32-S-2
14	66.2	ND	92.85	---	---	54999-32-S-3
16	65.65	ND	90.90	1.10E+03	---	54999-32-S-4
18	65.8	ND	89.50	---	---	54999-32-S-5
20	65.41	ND	88.83	3.50E+04	---	54999-32-S-6
22	65.41	ND	91.29	---	---	54999-32-S-7
24	65.3	0.3	83.42	2.60E+05	YES	54999-32-S-9
24	64.65	0.4	83.83	1.70E+04	YES	54999-32-S-8
38	11.48	37.4	68.79	---	---	54999-32-S-10
284	ND	ND	41.42	---	---	54999-32-S-11
Replicate 2						
0	71.04	ND	102.37	4.50E+02	---	54999-34-S-1
12	69.74	ND	99.48	---	---	54999-34-S-2
14	69.09	ND	93.69	---	---	54999-34-S-3
16	68.66	ND	90.85	3.30E+03	---	54999-34-S-4
18	68.16	ND	90.37	---	---	54999-34-S-5
20	67.37	ND	89.83	3.30E+03	---	54999-34-S-6
22	67.03	ND	83.94	---	---	54999-34-S-7
24	65.44	ND	75.92	2.40E+04	YES	54999-34-S-8
24	72.42	ND	83.12	---	YES	54999-34-S-9
38	22.84	27.84	33.13	---	---	54999-34-S-10
284	ND	18.36	3.66	---	---	54999-34-S-11

Table A.3. H4-4 Inhibition Test 1, Replicates 1 and 2.

Replicate 1

Time (h)	NO ₃ (mg/L)	NO ₂ (mg/L)	Acetate (mg/L)	CFU (#/mL)	QA Sample	Sample ID
0	62.23	1.69	79.76	---	---	5499-8-H-1
2	61.88	2.13	79.58	---	---	5499-8-H-2
4	62.13	1.67	78.55	3.30E+03	YES	5499-8-H-3
4	61.85	1.25	72.64	---	YES	5499-8-H-8
6	61.99	1.08	74.84	---	---	5499-8-H-4
8	62.12	0.82	75.04	3.30E+03	---	5499-8-H-5
10	61.75	ND	77.99	---	---	5499-8-H-6
12	61.5	2.87	71.33	3.50E+05	---	5499-8-H-7
101	49.81	---	---	5.40E+06	---	5499-8-H-9
146	49.39	0.32	---	---	---	5499-8-H-10
173	49.19	0.32	---	---	---	5499-8-H-11
199	49.29	0.41	---	---	---	5499-8-H-12
263	50.12	4.63	---	---	---	5499-8-H-13

Replicate 2

0	61.79	1.28	78.66	---	---	5499-10-H-1
2	61.8	0.83	78.34	---	---	5499-10-H-2
4	61.96	1.04	76.49	2.40E+04	---	5499-10-H-3
6	61.82	0.97	79.28	---	---	5499-10-H-4
8	61.65	0.81	78.41	2.20E+05	YES	5499-10-H-5
8	61.69	0.82	74.8	1.70E+04	YES	5499-10-H-8
10	61.7	0.92	78.32	---	---	5499-10-H-6
12	61.18	2.94	77.5	5.40E+05	---	5499-10-H-7

COMMENTS: Although these data are labeled an inhibitory test, the test was run before initiating adding phosphate to the media to ensure that there were no phosphate limitations.

Table A.4. H4-4 Inhibition Test 2, Replicates 1 and 2.

Time (h)	NO ₃ (mg/L)	NO ₂ (mg/L)	Acetate (mg/L)	CFU (#/mL)	QA Sample	Sample ID
Replicate 1						
0	94.24	ND	89.24	2.00E+02	---	54999-28-H-1
12	92.95	ND	84.23	4.00E+02	---	54999-28-H-2
14	92.4	ND	84.47	---	---	54999-28-H-3
16	92.39	ND	83.06	3.20E+03	---	54999-28-H-4
18	92.17	ND	83.22	---	---	54999-28-H-5
20	92.69	ND	76.81	2.10E+04	YES	54999-28-H-9
20	91.96	ND	82.48	3.90E+03	YES	54999-28-H-6
22	91.75	0.35	82.48	---	---	54999-28-H-7
24	91.35	0.67	76.54	1.40E+05	---	54999-28-H-8
38	65.05	24.72	78.93	---	---	54999-28-H-10
284	ND	ND	12.4	---	---	54999-28-H-11
Replicate 2						
0	93.67	ND	90.01	1.30E+03	---	54999-30-H-1
12	91.18	ND	80.71	2.10E+04	---	54999-30-H-2
14	90.46	ND	75	---	---	54999-30-H-3
16	90.39	ND	72.61	3.30E+04	---	54999-30-H-4
18	89.88	ND	71.63	---	---	54999-30-H-5
20	89.75	0.2	73.42	1.70E+05	YES	54999-30-H-6
20	89.18	0.24	64.21	---	YES	54999-30-H-9
22	89.71	0.24	72.84	---	---	54999-30-H-7
24	89.33	0.48	65.54	2.50E+03	---	54999-30-H-8
38	83.08	5.08	65.24	---	---	54999-30-H-10
284	ND	12.43	5.77	---	---	54999-30-H-11

COMMENTS: Two plots are shown: 1) with the full data set to 288 h, and 2) data plotted in the standard 156 h format.

Table A.5. D5-15 Inhibition Test 1, Replicates 1 and 2.

Replicate 1

Time (h)	NO ₃ (mg/L)	NO ₂ (mg/L)	Acetate (mg/L)	CFU (#/mL)	QA Sample	Sample ID
0	47.44	1.11	65.02	---	---	54999-4-D-1
2	45.75	1.53	63.65	---	YES	54999-4-D-2
2	47.22	1.39	61.97	---	YES	54999-4-D-8
4	45.95	1.16	62.72	1.30E+03	---	54999-4-D-3
6	47.23	1.46	65.15	---	---	54999-4-D-4
8	47.33	0.80	63.32	7.90E+03	---	54999-4-D-5
10	47.38	0.93	62.17	---	---	54999-4-D-6
12	47.25	1.40	58.96	4.90E+03	---	54999-4-D-7
101	37.87	---	---	3.10E+04	---	54999-4-D-9
146	37.67	---	---	---	---	54999-4-D-10
173	37.54	---	---	---	---	54999-4-D-11
199	37.55	---	---	---	---	54999-4-D-12
263	37.66	---	---	---	---	54999-4-D-13

Replicate 2

0	47.21	1.35	67.03	---	---	54999-6-D-1
2	47.28	1.17	67.14	---	---	54999-6-D-2
4	48.15	1.06	65.95	1.70E+04	YES	54999-6-D-3
4	47.14	0.82	62.44	3.30E+03	YES	54999-6-D-8
6	47.28	1.14	66.20	---	---	54999-6-D-4
8	47.29	1.25	67.06	7.00E+03	---	54999-6-D-5
10	47.12	0.92	63.96	---	---	54999-6-D-6
12	47.01	1.80	63.12	2.20E+03	---	54999-6-D-7
101	37.50	---	---	---	---	54999-6-D-9
146	37.23	---	---	---	---	54999-6-D-10
173	37.27	---	---	---	---	54999-6-D-11
199	37.25	---	---	---	---	54999-6-D-12
263	37.21	---	---	---	---	54999-6-D-13

Table A.6. D5-15 Inhibition Test 2, Replicates 1 and 2.

Time (h)	NO ₃ (mg/L)	NO ₂ (mg/L)	Acetate (mg/L)	CFU (#/mL)	QA Sample	Sample ID
Replicate 1						
0	48.85	ND	92.83	---	---	54999-24-D-1
12	48.41	ND	90.34	6.10E+02	---	54999-24-D-2
14	48.2	ND	89.64	---	YES	54999-24-D-3
14	47.98	ND	83.00	---	YES	54999-24-D-9
16	48.13	ND	88.61	2.10E+03	---	54999-24-D-4
18	47.86	ND	87.88	---	---	54999-24-D-5
20	47.53	ND	84.09	1.40E+04	---	54999-24-D-6
22	47.53	ND	86.32	---	---	54999-24-D-7
24	47.14	ND	81.96	1.70E+04	---	54999-24-D-8
38	46.76	0.28	85.69	---	---	54999-24-D-10
263	ND	ND	51.32	---	---	54999-24-D-11
Replicate 2						
0	48.55	ND	86.96	6.80E+02	---	54999-26-D-1
12	48.17	ND	87.62	1.10E+03	---	54999-26-D-2
14	47.33	ND	82.72	---	---	54999-26-D-3
16	47.36	ND	83.42	4.90E+03	YES	54999-26-D-4
16	47.2	ND	77.33	-	YES	54999-26-D-9
18	46.95	ND	81.02	---	---	54999-26-D-5
20	46.55	ND	79.83	3.90E+03	---	54999-26-D-6
22	46.64	ND	80.28	---	---	54999-26-D-7
24	46.19	ND	75.19	1.70E+04	---	54999-26-D-8
38	46.28	ND	78.54	---	---	54999-26-D-10
284	ND	ND	44.8	---	---	54999-26-D-11

COMMENTS: Noise in the acetate data is compounded by plotting both sets of replicate data on the same plot.

Table A.7. D5-15 Inhibition Test 3, Replicates 1 and 2.

Time (h)	NO ₃ (mg/L)	NO ₂ (mg/L)	Acetate (mg/L)	CFU (#/mL)	QA Sample	Sample ID
Replicate 1						
0	51.12	ND	78.51	---	---	54999-66-D-1
24	50.94	ND	77.80	6.10E+02	---	54999-66-D-2
48	42.72	0.75	60.58	---	---	54999-66-D-3
64	33.49	0.65	51.31	---	---	54999-66-D-4
72	31.09	0.73	45.81	2.10E+03	---	54999-66-D-5
88	25.46	0.44	30.84	---	---	54999-66-D-6
96	23.33	0.10	26.48	1.40e+04	---	54999-66-D-7
164	9.33	ND	3.56	---	---	54999-66-D-8
Replicate 2						
0	51.31	ND	78.52	6.80E+02	---	54999-68-D-1
24	51.15	ND	77.54	1.10E+03	---	54999-68-D-2
48	31.30	ND	55.40	---	---	54999-68-D-3
64	8.46	ND	35.95	4.90E+03	YES	54999-68-D-4
64	8.55	ND	35.83	---	YES	54999-68-D-10
72	ND	ND	28.45	---	---	54999-68-D-5
88	ND	ND	30.66	---	---	54999-68-D-6
96	ND	ND	30.65	3.90e+03	---	54999-68-D-7
164	ND	ND	31.20	---	---	54999-68-D-8

Table A.8. Composite Sample - pH 6, Replicate 1 and 2.

Time (h)	NO ₃ (mg/L)	NO ₂ (mg/L)	Acetate (mg/L)	CFU (#/mL)	QA Sample	Sample ID
Replicate 1						
0	81.19	ND	98.51	4.50E+02	---	54999-52-HD-1
12	81.42	ND	99.02	1.00E+00	---	54999-52-HD-2
18	81.64	ND	99.13	---	---	54999-52-HD-5
24	---	---	---	1.00E+00	---	54999-52-HD-8
26	81.64	ND	99.13	---	---	54999-52-HD-10
30	80.06	0.58	110.57	---	---	54999-52-HD-12
35	79.81	0.59	109.55	---	---	54999-52-HD-14
43	80.01	0	109.97	---	---	54999-52-HD-16
47	---	---	---	5.40E+06	---	54999-52-HD-17
51	75.68	1.02	95.44	---	---	54999-52-HD-18
86	0.1	59.35	51.75	---	---	54999-52-HD-20
Replicate 2						
0	79.85	ND	106.75	4.50E+02	---	54999-54-HD-1
12	81.06	ND	110.65	1.00E+00	---	54999-54-HD-2
18	80.11	ND	109.7	---	---	54999-54-HD-5
24	---	---	---	2.00E+02	---	54999-54-HD-8
26	---	---	---	1.00E+00	---	54999-54-HD-9
26	80.22	ND	106.75	---	---	54999-54-HD-10
30	80.76	ND	107.3	---	---	54999-54-HD-12
35	80.23	ND	107.88	---	---	54999-54-HD-14
43	80.83	ND	107.61	---	---	54999-54-HD-16
47	---	---	---	1.00E+00	---	54999-54-HD-17
51	80.77	ND	108.07	---	---	54999-54-HD-18
86	80.43	ND	107.72	---	---	54999-54-HD-20

9413221.0478

Table A.9. Composite Sample - pH 7, Replicates 1 and 2.

Time (h)	NO ₃ (mg/L)	NO ₂ (mg/L)	Acetate (mg/L)	CFU (#/mL)	QA Sample	Sample ID
Replicate 1						
0	82.08	ND	100.89	4.50E+02	---	54999-48-HD-1
12	80.65	ND	94.95	1.00E+03	---	54999-48-HD-2
18	80.38	ND	90.00	---	---	54999-48-HD-5
24	---	---	---	3.50E+05	---	54999-48-HD-8
26	78.37	ND	85.67	---	---	54999-48-HD-10
30	77.57	0.12	95.15	---	---	54999-48-HD-12
35	75.86	0.79	91.81	---	---	54999-48-HD-14
43	72.56	2.69	88.31	---	---	54999-48-HD-16
47	---	---	---	1.60E+07	---	54999-48-HD-17
51	49.33	12.82	73.54	---	---	54999-48-HD-18
86	0.34	26.88	36.15	---	---	54999-48-HD-20
Replicate 2.						
0	81.66	ND	---	7.80E+02	---	54999-50-HD-1
12	80.79	ND	---	3.50E+04	---	54999-50-HD-2
18	80	ND	---	---	---	54999-50-HD-5
24	---	---	---	3.50E+05	---	54999-50-HD-8
26	77.76	ND	96.29	---	---	54999-50-HD-10
30	78.91	0.38	95.33	---	---	54999-50-HD-12
35	75.81	1.33	93.25	---	---	54999-50-HD-14
43	66.88	6.67	88.16	---	---	54999-50-HD-16
47	---	---	---	1.60E+07	---	54999-50-HD-17
51	12.96	30.58	59.05	---	---	54999-50-HD-18
86	ND	ND	---	---	---	54999-50-HD-20

Table A.10. Composite Sample - pH 8, Replicate 1.

Time (h)	NO ₃ (mg/L)	NO ₂ (mg/L)	Acetate (mg/L)	CFU (#/mL)	QA Sample	Sample ID
0	78.73	ND	77.24	4.50E+02	---	54999-46-HD-1
12	77.03	ND	72.17	1.70E+04	---	54999-46-HD-2
14	76.79	ND	82.8	---	---	54999-46-HD-3
16	76.73	ND	82.26	---	---	54999-46-HD-4
18	76.63	ND	68.37	---	---	54999-46-HD-5
20	76.41	0.21	81.1	---	---	54999-46-HD-6
22	76.62	0.21	80.67	---	---	54999-46-HD-7
24	76.65	0.21	81.49	1.60E+05	---	54999-46-HD-8
---	76.74	0.21	82.17	---	---	54999-46-HD-9
26	75.58	0.21	78.62	---	---	54999-46-HD-10
28	75.94	0.21	78.76	---	---	54999-46-HD-11
30	75.58	0.21	80.27	---	---	54999-46-HD-12
32	75.85	0.43	79.56	---	---	54999-46-HD-13
35	75.06	0.53	77.37	---	YES	54999-46-HD-14
35	75.20	0.42	77.80	---	YES	54999-46-HD-19
39	74.09	0.75	76.74	---	---	54999-46-HD-15
43	72.52	1.07	77.52	---	---	54999-46-HD-16
47	70.76	1.43	76.24	1.60E+07	---	54999-46-HD-17
60	56.27	3.71	67.53	---	---	54999-46-HD-18
86	16	6.08	43.55	---	---	54999-46-HD-20

9473221.0480

Table A.11. Composite Sample - pH 8, Replicate 2.

Time (h)	NO ₃ (mg/L)	NO ₂ (mg/L)	Acetate (mg/L)	CFU (#/mL)	QA Sample	Sample ID
0	79.49	ND	86.11	---	---	54999-44-HD-1
12	77.68	ND	81.04	4.90E+03	YES	54999-44-HD-2
12	77.48	ND	76.22	---	YES	54999-44-HD-9
14	77.27	ND	79.63	---	---	54999-44-HD-3
16	77.42	ND	78.58	---	---	54999-44-HD-4
18	75.56	ND	73.59	---	---	54999-44-HD-5
20	74.58	ND	69.03	---	---	54999-44-HD-6
22	74.64	ND	63.23	---	---	54999-44-HD-7
24	73.58	ND	58.87	5.40E+06	---	54999-44-HD-8
26	72.51	ND	53.08	---	---	54999-44-HD-10
28	72.10	ND	50.36	---	---	54999-44-HD-11
30	67.37	ND	33.25	---	---	54999-44-HD-12
32	65.30	ND	14.50	---	---	54999-44-HD-13
35	61.62	ND	2.01	---	---	54999-44-HD-14
39	62.12	ND	2.09	---	---	54999-44-HD-15
43	62.76	ND	2.40	---	---	54999-44-HD-16
47	62.31	ND	2.01	1.60E+07	---	54999-44-HD-17
60	62.25	ND	1.47	---	---	54999-44-HD-18
86	62.12	ND	2.09	---	---	54999-44-HD-20

Table A.12. Composite Sample - 15°C, Replicate 1 and 2.

Time (h)	NO ₃ (mg/L)	NO ₂ (mg/L)	Acetate (mg/L)	CFU (#/mL)	QA Sample	Sample ID
Replicate 1						
0	55.32	---	79.42	9.20E+04	YES	54999-82-HD-1
0	55.07	---	76.72	7.00E+04	YES	54999-82-HD-1
24	55.18	---	80.63	---	---	54999-82-HD-2
48	54.23	---	75.49	3.30E+03	---	54999-82-HD-3
72	43.08	---	57.13	---	---	54999-82-HD-4
96	22.06	---	41.17	2.00E+02	---	54999-82-HD-5
163	ND	---	16.37	---	---	54999-82-HD-8
187	ND	---	17.19	1.60E+06	---	54999-82-HD-9
211	ND	---	17.99	1.60E+06	---	54999-82-HD-1
235	ND	---	18.53	---	---	54999-82-HD-1
Replicate 2						
0	55.2	---	76.7	9.20E+04	YES	54999-84-HD-1
0	55.22	---	76.13	---	YES	54999-84-HD-1
24	55.09	---	77.35	---	---	54999-84-HD-2
48	54.02	---	72.57	3.30E+03	---	54999-84-HD-3
48	---	---	---	1.30E+03	---	54999-84-HD-1
72	45.25	---	61.31	---	---	54999-84-HD-4
96	26.06	---	45.52	2.30E+03	---	54999-84-HD-5
163	ND	---	17.97	---	---	54999-84-HD-8
187	ND	---	18.81	1.60E+07	---	54999-84-HD-9
211	ND	---	19.76	1.60E+07	---	54999-84-HD-1
235	ND	---	20.03	---	---	54999-84-HD-1

Table A.13. Composite Sample - 35°C, Replicates 1 and 2.

Time (h)	NO ₃ (mg/L)	NO ₂ (mg/L)	Acetate (mg/L)	CFU (#/mL)	QA Sample	Sample ID
Replicate 1						
0	56.93	ND	71.75	2.00E+02	---	54999-58-HD-1
16	56.53	ND	68.85	3.10E+04	---	54999-58-HD-2
24	47.74	4.95	64.85	---	---	54999-58-HD-3
32	20.35	22.04	54.83	---	YES	54999-58-HD-4
32	20.21	22.12	52.75	1.60E+07	YES	54999-58-HD-7
42	0.1	29.67	42.96	---	---	54999-58-HD-5
50	ND	19.31	37.15	2.40E+04	---	54999-58-HD-6
Replicate 2						
0	57.1	ND	72.64	4.00E+02	---	54999-60-HD-1
16	55.83	ND	67.36	4.60E+03	---	54999-60-HD-2
24	44.94	6.7	59.66	---	---	54999-60-HD-3
32	15.73	25.1	49.57	---	---	54999-60-HD-4
42	ND	30.43	41.72	---	---	54999-60-HD-5
50	ND	21.44	35.28	3.50E+04	---	54999-60-HD-6

5810 1726 116

Table A.14. Composite Sample - 2/3 Stoichiometric Ratio, Replicate 1 and 2.

Time (h)	NO ₃ (mg/L)	NO ₂ (mg/L)	Acetate (mg/L)	CFU (#/mL)	QA Sample	Sample ID
Replicate 1						
0	56.98	ND	46.36	3.30E+03	YES	54999-74-HD-1
0	56.6	ND	42.26	---	YES	54999-74-HD-2
48	30.26	ND	6.66	1.60E+06	---	54999-74-HD-3
64	22.42	ND	1.89	---	---	54999-74-HD-4
72	21.97	ND	2.81	---	---	54999-74-HD-5
88	22.02	ND	1.59	1.60E+07	---	54999-74-HD-6
96	21.72	ND	2.43	---	YES	54999-74-HD-7
96	21.84	ND	ND	---	YES	54999-74-HD-10
164	21.61	ND	1.86	1.60E+07	---	54999-74-HD-8
Replicate 2						
0	57.1	ND	44.49	1.70E+03	---	54999-76-HD-1
24	56.92	ND	43.86	---	---	54999-76-HD-2
48	33.3	ND	12.97	3.60E+04	---	54999-76-HD-3
64	19.72	0.9	2.74	---	---	54999-76-HD-4
72	19.82	ND	3.38	---	---	54999-76-HD-5
88	19.52	ND	3.2	1.60E+07	---	54999-76-HD-6
96	19.66	ND	2.9	---	---	54999-76-HD-7
164	19.48	ND	2.17	1.60E+07	YES	54999-76-HD-8
164	19.41	ND	0.1	1.10E+05	YES	54999-76-HD-10

Table A.15. Composite Sample - 1/1 Stoichiometric Ratio, Replicate 1 and 2.

Time (h)	NO ₃ (mg/L)	NO ₂ (mg/L)	Acetate (mg/L)	CFU (#/mL)	QA Sample	Sample ID
Replicate 1						
0	57.19	ND	54.03	---	---	54999-78-HD-1
24	56.62	ND	52.49	---	YES	54999-78-HD-2
24	56.48	ND	51.61	---	YES	54999-78-HD-10
48	45.64	1.05	5.79	---	---	54999-78-HD-3
64	42.8	1.57	3.06	1.60E+07	---	54999-78-HD-4
72	42.27	1.68	2.31	---	---	54999-78-HD-5
88	41.77	1.39	2.91	---	---	54999-78-HD-6
96	41.76	1.39	2.79	---	---	54999-78-HD-7
164	41.52	ND	3.23	---	---	54999-78-HD-8
Replicate 2						
0	57.25	ND	56.65	---	---	54999-80-HD-1
24	56.64	ND	56.18	---	---	54999-80-HD-2
48	23.81	ND	18.13	1.60E+07	---	54999-80-HD-3
48	23.64	ND	18.03	1.60E+07	YES	54999-80-HD-10
64	6.24	ND	2.91	---	YES	54999-80-HD-4
72	6.08	ND	2.73	---	---	54999-80-HD-5
88	6.06	ND	2.23	1.60E+07	---	54999-80-HD-6
96	6.02	ND	3.17	---	---	54999-80-HD-7
164	6.05	ND	2.99	9.20E+06	---	54999-80-HD-8

5840-2246

Table A.16. Composite Sample - Large Volume Denitrification.

Time (h)	NO ₃ (mg/L)	NO ₂ (mg/L)	MeOH (mg/L)	CFU (#/mL)	QA Sample	Sample ID
0	27.8	0.04	23.88	4.60E+03	YES	54996-29-1
0	39.08	0.04	23.77	---	YES	54996-29-1
22.5	35.38	0.04	0.00	3.50E+05	YES	54996-29-2
22.5	43.31	0.04	0.00	---	YES	54996-29-2
46.5	40.56	0.04	40.12	---	YES	54996-30-3
46.5	---	---	40.00	---	YES	54996-30-3
70.5	36.71	0.04	35.83	---	YES	54996-30-4
70.5	---	---	35.79	---	YES	54996-30-4
94.5	37.16	0.4	16.58	1.60E+06	YES	54996-30-5
94.5	---	---	14.70	---	YES	54996-30-5
118.5	27.99	0.62	0.00	---	YES	54996-31-6
118.5	---	---	0.00	---	YES	54996-31-6
142.5	30.1	0.61	0.69	2.80E+05	YES	54996-31-7
142.5	---	---	0.68	---	YES	54996-31-7
166.5	30.22	0.54	0.00	---	YES	54996-32-8
166.5	---	---	0.00	---	YES	54996-32-8
190.5	31.51	0.54	0.00	3.50E+05	YES	54996-33-9
190.5	---	---	0.00	---	YES	54996-33-9
214	30.27	0.51	0.00	---	YES	54996-34-10
214	---	---	0.00	---	YES	54996-34-10
286	18.34	6.09	0.00	---	YES	54996-36-11
286	---	---	0.00	---	YES	54996-36-11
310.5	18.23	6.07	0.42	9.20E+05	YES	54996-37-12
310.5	---	---	0.43	---	YES	54996-37-12
334	17.98	6.03	0.00	---	YES	54996-37-13
334	---	---	0.00	---	YES	54996-37-13
358.5	12.11	9.36	41.05	1.60E+06	YES	54996-38-14
358.5	---	---	41.89	---	YES	54996-38-14
374.5	0.28	15.99	25.03	---	YES	54996-39-15
374.5	---	---	25.28	---	YES	54996-39-15

Table A.17. Composite Sample - MeOH growth, Test 1, Replicates 1 and 2.

Time (h)	NO ₃ (mg/L)	NO ₂ (mg/L)	MeOH (mg/L)	CFU (#/mL)	QA Sample	Sample ID
Replicate 1						
0	56.75	ND	---	2.00E+02	---	54999-70-HD-1
24	56.51	ND	---	---	---	54999-70-HD-2
48	55.61	ND	---	3.50E+04	---	54999-70-HD-3
64	52.35	0.42	---	---	---	54999-70-HD-4
72	50.35	0.49	---	---	YES	54999-70-HD-5
72	50.37	0.48	---	---	YES	54999-70-HD-10
88	46.1	0.78	---	1.60E+04	---	54999-70-HD-6
96	43.33	1.08	---	---	---	54999-70-HD-7
164	ND	7.73	---	1.40E+05	---	54999-70-HD-8
Replicate 2						
0	56.54	ND	---	2.00E+02	---	54999-72-HD-1
24	56.4	ND	---	---	---	54999-72-HD-2
48	55.45	ND	---	9.20E+04	---	54999-72-HD-3
64	52.69	0.72	---	---	---	54999-72-HD-4
72	51.05	0.85	---	---	---	54999-72-HD-5
88	47.39	1.46	---	3.50E+06	YES	54999-72-HD-6
88	47.09	1.44	---	1.70E+05	YES	54999-72-HD-10
96	44.85	1.92	---	---	---	54999-72-HD-7
164	ND	22.02	---	2.40E+04	---	54999-72-HD-8

Table A.18. Composite Sample - MeOH growth, Test 2, Replicates 1 and 2.

<u>Time</u> <u>(h)</u>	<u>NO₃</u> <u>(mg/L)</u>	<u>NO₂</u> <u>(mg/L)</u>	<u>MeOH</u> <u>(mg/L)</u>	<u>CFU</u> <u>(#/mL)</u>	<u>QA</u> <u>Sample</u>	<u>Sample ID</u>
Replicate 1						
0	---	---	---	1.20E+02	---	54999-86-HD-1
44	---	---	---	2.30E+02	---	54999-86-HD-3
67	---	---	---	7.00E+02	YES	54999-86-HD-5
67	---	---	---	1.30E+03	YES	54999-86-HD-13
91	---	---	---	1.80E+03	---	54999-86-HD-7
115	---	---	---	1.60E+04	---	54999-86-HD-9
139	---	---	---	3.50E+03	---	54999-86-HD-11
147	---	---	---	7.00E+03	---	54999-86-HD-12
Replicate 2						
0	---	---	---	3.30E+02	---	54999-88-HD-1
44	---	---	---	2.30E+02	---	54999-88-HD-3
67	---	---	---	2.60E+03	---	54999-88-HD-5
91	---	---	---	1.40E+03	YES	54999-88-HD-7
91	---	---	---	1.30E+03	YES	54999-88-HD-13
115	---	---	---	4.60E+03	---	54999-88-HD-9
139	---	---	---	1.10E+04	---	54999-88-HD-11
147	---	---	---	6.40E+03	---	54999-88-HD-12

Table A.19. Composite Sample, Final Confirmation Tests Using MeOH, Replicates 1 and 2.

Time (h)	NO ₃ (mg/L)	NO ₂ (mg/L)	MeOH (mg/L)	CFU (#/mL)	QA Sample	Sample ID
Replicate 1						
0	46.44	0	---	---	---	54999-96-1
48	30.37	0	55.673	---	YES	54999-96-3
48	---	---	53.013	---	YES	54999-96-3
97	32.68	11.69	31.999	---	YES	54999-96-7
97	---	---	31.999	---	YES	54999-96-7
135	0.78	19.02	---	---	---	54999-96-10
159	0.58	15.55	11.656	---	YES	54999-96-12
159	---	---	11.888	---	YES	54999-96-12
Replicate 2						
0	47.19	0	---	---	---	54999-98-1
48	47.7	0	57.21	---	YES	54999-98-3
48	---	---	57.309	---	YES	54999-98-3
97	30.2	11.45	51.73	---	YES	54999-98-7
97	---	---	51.724	---	YES	54999-98-7
135	8.92	25.19	---	---	---	54999-98-10
159	0.73	23.15	37.869	---	YES	54999-98-12
159	---	---	37.945	---	---	54999-98-12

Comments: Replicates 1 and 2 were sampled less frequently, than replicates 3 to 6 since split samples were taken and sent to the PNL 325 Analytical Laboratory for external laboratory confirmation of analytical results. A comparison between in-house and external analytical results is given in Table B.2. CFU (#/mL) data was discarded for these tests because of a high degree of visually observed cell clumping. Observed CFU data values were 2 to 4 orders of magnitude lower than expected, based both on the denitrification rate and the measured Total Suspended Solids (Table B.3).

Table A.20. Composite Sample, Final Confirmation Tests Using MeOH, Replicate 3.

<u>Time</u> <u>(h)</u>	<u>NO₃</u> <u>(mg/L)</u>	<u>NO₂</u> <u>(mg/L)</u>	<u>MeOH</u> <u>(mg/L)</u>	<u>CFU</u> <u>(#/mL)</u>	<u>QA</u> <u>Sample</u>	<u>Sample ID</u>
Replicate 3						
0	43.78	0	58.85	---	YES	54999-100-1
0	---	---	58.90	---	YES	54999-100-1
0	48.58	0	---	---	YES	54999-100-13
24	53.57	0	59.95	---	YES	54999-100-2
24	---	---	59.434	---	YES	54999-100-2
48	48.09	0	55.052	---	YES	54999-100-3
48	---	---	55.281	---	YES	54999-100-3
64	48.63	1.72	52.461	---	YES	54999-100-4
64	---	---	52.71	---	YES	54999-100-4
73	36.44	3.62	47.207	---	YES	54999-100-5
73	---	---	48.5	---	YES	54999-100-5
73	44.05	4.44	47.282	---	YES	54999-100-14
73	---	---	47.312	---	YES	54999-100-14
87	31.59	9.42	42.386	---	YES	54999-100-6
87	---	---	42.276	---	YES	54999-100-6
97	20.58	8.63	34.406	---	YES	54999-100-7
97	---	---	35.929	---	YES	54999-100-7
111	9.1	21.3	29.592	---	YES	54999-100-8
111	---	---	29.499	---	YES	54999-100-8
121	5.72	20.31	19.12	---	YES	54999-100-9
121	---	---	19.168	---	YES	54999-100-9
121	6.33	21.91	19.584	---	YES	54999-100-15
121	---	---	19.552	---	YES	54999-100-15
135	1.09	23.05	---	---	---	54999-100-10
145	1.17	22.8	0.892	---	YES	54999-100-11
145	---	---	1.532	---	YES	54999-100-11
159	0.89	14.5	0.587	---	YES	54999-100-12
159	---	---	0.358	---	YES	54999-100-12

Table A.21. Composite Sample, Final Confirmation Tests Using MeOH, Replicate 4.

Time (h)	NO ₃ (mg/L)	NO ₂ (mg/L)	MeOH (mg/L)	CFU (#/mL)	QA Sample	Sample ID
Replicate 4						
0	46.33	0	---	---	---	54999-102-1
24	41.17	0	56.241	---	YES	54999-102-2
24	---	---	40.177	---	YES	54999-102-2
48	57.99	0.97	55.883	---	YES	54999-102-3
48	---	---	55.779	---	YES	54999-102-3
64	47.54	4.09	54.721	---	YES	54999-102-4
64	---	---	54.343	---	YES	54999-102-4
73	37.84	6	52.577	---	YES	54999-102-5
73	---	---	51.107	---	YES	54999-102-5
87	29.9	9.14	49.888	---	YES	54999-102-6
87	---	---	49.268	---	YES	54999-102-6
97	23.67	10.78	45.96	---	YES	54999-102-7
97	---	---	45.904	---	YES	54999-102-7
111	18.48	17.17	43.177	---	YES	54999-102-8
111	---	---	43.302	---	YES	54999-102-8
121	11.04	19.92	40.752	---	YES	54999-102-9
121	---	---	41.42	---	YES	54999-102-9
135	2.01	25.32	---	---	YES	54999-102-10
135	2.24	26.84	---	---	YES	54999-102-15
145	1.01	26.01	36.945	---	YES	54999-102-11
145	---	---	36.868	---	YES	54999-102-11
159	0.79	24.89	35.716	---	YES	54999-102-12
159	---	---	35.766	---	YES	54999-102-12
24	---	---	56.857	---	YES	54999-102-13
24	---	---	56.784	---	YES	54999-102-13
87	34.99	10.53	50.194	---	YES	54999-102-14
87	---	---	50.438	---	YES	54999-102-14

Table A.22. Composite Sample, Final Confirmation Tests Using MeOH, Replicate 5.

Time (h)	NO ₃ (mg/L)	NO ₂ (mg/L)	MeOH (mg/L)	CFU (#/mL)	QA Sample	Sample ID
Replicate 5						
0	45.19	0	---	---	---	54999-104-1
24	54.5	0	57.987	---	YES	54999-104-2
24	---	---	58.13	---	YES	54999-104-2
48	31.57	0.45	55.808	---	YES	54999-104-3
48	---	---	56.008	---	YES	54999-104-3
64	40.77	3.04	55.339	---	YES	54999-104-4
64	---	---	54.639	---	YES	54999-104-4
73	38.88	4.67	52.185	---	YES	54999-104-5
73	---	---	51.95	---	YES	54999-104-5
87	35.83	6.89	51.776	---	YES	54999-104-6
87	---	---	52.038	---	YES	54999-104-6
97	34.32	8.99	49.873	---	YES	54999-104-7
97	---	---	50.725	---	YES	54999-104-7
97	37.79	9.78	49.448	---	YES	54999-104-14
111	26.75	10.56	48.94	---	YES	54999-104-8
111	---	---	48.885	---	YES	54999-104-8
121	26.13	14.72	47.2	---	YES	54999-104-9
121	---	---	47.79	---	YES	54999-104-9
135	17.03	17.15	43.478	---	---	54999-104-10
145	10.37	16.02	---	---	YES	54999-104-11
145	15.29	23.41	41.932	---	YES	54999-104-15
145	---	---	41.928	---	YES	54999-104-15
159	8.98	26.51	---	---	---	54999-104-12

Table A.23. Composite Sample, Final Confirmation Tests Using MeOH, Replicate 6.

Time (h)	NO ₃ (mg/L)	NO ₂ (mg/L)	MeOH (mg/L)	CFU (#/mL)	QA Sample	Sample ID
Replicate 6						
0	29.56	0	---	---	---	54999-106-1
24	44.85	0	---	---	---	54999-106-2
48	35.38	0.42	---	---	---	54999-106-3
64	53.94	2.24	56.707	---	---	54999-106-4
73	42.68	2.99	56.486	---	YES	54999-106-5
73	---	---	56.183	---	YES	54999-106-5
87	39.49	5.05	55.031	---	YES	54999-106-6
87	---	---	55.149	---	YES	54999-106-6
97	31.19	5.98	53.663	---	YES	54999-106-7
97	---	---	53.241	---	YES	54999-106-7
111	27.7	9.28	51.116	---	YES	54999-106-8
111	---	---	50.258	---	YES	54999-106-8
121	16.69	8.37	48.965	---	YES	54999-106-9
121	---	---	49.323	---	YES	54999-106-9
121	28.39	9.65	49.76	---	YES	54999-106-14
121	---	---	50.083	---	YES	54999-106-14
135	10.7	14.63	---	---	---	54999-106-10
145	0.51	1.96	42.646	---	YES	54999-106-11
145	---	---	42.845	---	YES	54999-106-11
159	0.6	21.22	39.355	---	YES	54999-106-12
159	---	---	39.154	---	YES	54999-106-12
159	0.73	21.97	39.771	---	YES	54999-106-15
159	---	---	39.616	---	YES	54999-106-15

Table A.24. SGW with no Bacteria Added.

<u>Time</u> <u>(h)</u>	<u>NO₃</u> <u>(mg/L)</u>	<u>NO₂</u> <u>(mg/L)</u>	<u>Acetate</u> <u>(mg/L)</u>	<u>CFU</u> <u>(#/mL)</u>	<u>QA</u> <u>Sample</u>	<u>Sample ID</u>
0	67.89	ND	98.96	ND	YES	54999-36-B-1
12	67.76	ND	98.64	ND	YES	54999-36-B-2
14	67.73	ND	98.48	ND	YES	54999-36-B-3
16	67.73	ND	97.98	ND	YES	54999-36-B-4
18	67.46	ND	97.31	ND	YES	54999-36-B-5
20	67.58	ND	96.38	ND	YES	54999-36-B-6
22	67.78	ND	96.75	ND	YES	54999-36-B-7
24	67.03	ND	96.7	ND	YES	54999-36-B-8
284	67.56	ND	98.79	ND	YES	54999-36-B-10

9/13/22, 09:04

Table A.25. D5-15, No Carbon Source, Control.

Time (h)	NO ₃ (mg/L)	NO ₂ (mg/L)	Acetate (mg/L)	CFU (#/mL)	QA Sample	Sample ID
0	50.11	ND	ND	4.50E+02	YES	54999-40-D-1
12	50.03	ND	ND	6.80E+02	YES	54999-40-D-2
14	50.02	ND	ND	---	YES	54999-40-D-3
16	50.01	ND	ND	---	YES	54999-40-D-4
18	50.18	ND	ND	1.00E+00	YES	54999-40-D-5
20	49.94	ND	ND	---	YES	54999-40-D-6
22	50.04	ND	ND	---	YES	54999-40-D-7
24	49.82	ND	ND	1.10E+03	YES	54999-40-D-8
12	49.75	ND	ND	4.50E+02	YES	54999-40-D-9
26	49.87	ND	ND	---	YES	54999-40-D-10
28	49.79	ND	ND	---	YES	54999-40-D-11
30	49.87	ND	ND	---	YES	54999-40-D-12
32	49.72	ND	ND	---	YES	54999-40-D-13
35	49.86	ND	ND	---	YES	54999-40-D-14
39	49.84	ND	ND	---	YES	54999-40-D-15
43	49.96	ND	1.38	---	YES	54999-40-D-16
47	49.67	ND	ND	7.80E+02	YES	54999-40-D-17
60	50.59	ND	1.31	---	YES	54999-40-D-18
86	49.79	ND	-	---	YES	54999-40-D-20

5670-1728-146

Table A.26. D5-15, No Carbon Source, Control.

Time (h)	NO ₃ (mg/L)	NO ₂ (mg/L)	Acetate (mg/L)	CFU (#/mL)	QA Sample	Sample ID
0	50.53	ND	1.16	4.00E+02	YES	54999-42-D-1
12	50.27	ND	ND	7.80E+02	YES	54999-42-D-2
14	50.66	ND	1.03	---	YES	54999-42-D-3
16	49.94	ND	ND	---	YES	54999-42-D-4
18	50.24	ND	1.18	---	YES	54999-42-D-5
20	50.34	ND	ND	---	YES	54999-42-D-6
22	50.45	ND	ND	---	YES	54999-42-D-7
24	50.23	ND	ND	2.20E+03	YES	54999-42-D-8
12	50.23	ND	ND	---	YES	54999-42-D-9
26	50.49	ND	ND	---	YES	54999-42-D-10
28	47.72	ND	ND	---	YES	54999-42-D-11
30	50.18	ND	ND	---	YES	54999-42-D-12
32	50.27	ND	ND	---	YES	54999-42-D-13
35	50.38	ND	ND	---	YES	54999-42-D-14
39	50.28	ND	ND	---	YES	54999-42-D-15
43	49.98	ND	ND	---	YES	54999-42-D-16
47	50.23	ND	ND	1.30E+04	YES	54999-42-D-17
60	50.02	ND	ND	---	YES	54999-42-D-18
86	50.32	ND	ND	---	YES	54999-42-D-20

9/17/2016 12:22:04 PM

**THIS PAGE INTENTIONALLY
LEFT BLANK**

APPENDIX B
325 LABORATORY RESULTS

2022-09-27

Appendix B
325 Laboratory Results

941322.098

Table B.1. Biological Chromium and Radionuclide Removal from Composite Groundwater from Wells 199-H4-4 and 199-D5-15. Values are Average \pm 68% Confidence Value.

	<u>Before Filtration</u>	<u>After Filtration</u>	<u>Average % Removal</u>
<u>Total Chromium</u> ($\mu\text{g Cr/L}$)	990 \pm 80	980 \pm 80	1.5
	990 \pm 80	970 \pm 80	
<u>Gross Alpha</u> (pCi/L)	8.2 \pm 1.9	5.4 \pm 1.5	25
	6.2 \pm 1.8	5.4 \pm 1.6	
<u>Gross Beta</u> (pCi/L)	32.5 \pm 2.2	29.2 \pm 2.2	3.0
	29.6 \pm 2.1	31.3 \pm 2.1	

 661072616
 947321.0499

Table B.2. Comparison of Nitrate and Nitrite Results from Independent Laboratory Analyses.

Sample ID	PNL 324 Nitrate (mg/L)	PNL 325 Nitrate (mg/L)	Relative Percent Difference	PNL 324 Nitrite (mg/L)	PNL 325 Nitrite (mg/L)	Relative Percent Difference
96-HD-1	46.4	42	10.0	<1.0	< 2.5	NC
96-HD-3	30.4	42	32.0	<1.0	< 2.5	NC
96-HD-3D	-	43	-	-	< 2.5	-
96-HD-7	32.7	18	58.0	11.7	7	50.3
96-HD-10	<1.0	< 2.5	NC	19.0	17	11.1
96-HD-12	<1.0	< 2.5	NC	15.6	13	18.2
96-HD-13	-	42	-	-	< 2.5	-
98-HD-1	47.2	43	9.3	<1.0	< 2.5	NC
98-HD-3	47.7	47	1.5	<1.0	< 2.5	NC
98-HD-7	30.2	26	14.9	11.5	11	4.4
98-HD-10	8.9	6.4	32.7	25.2	21	18.2
98-HD-12	<1.0	< 2.5	NC	23.15	20	14.6

APPENDIX C
SUSPENDED SOLIDS RESULTS AND OBSERVATIONS

947322.550

2025-07-27
09:22:30Z

Table C.1. Total Suspended Solids (TSS) Raw Data for the Final Confirmation Tests.
Sample Volume was 100 mL.

<u>Dish ID</u>	<u>Tare Wt.(mg)</u>	<u>Final Wt. (mg)</u>	<u>TSS (mg/L)</u>
1	1965.1	1965.8	7
2	1983.3	1984.5	12
3	1974.2	1975.0	8
4	2004.0	2004.5	5
5	1975.9	1976.8	9
6	1991.3	1992.7	14
7	1993.2	1994.3	11

AVERAGE = 9.4
STD.DEV. = 3.1

Table C.2. Qualitative Observations Regarding Settling Characteristics of the Produced Biological Solids in the Final Confirmation Tests.

This information is taken from the lab record book #BNW54996. Liquid from the Final Confirmation tests, which used methanol as the carbon source, was used to fill a 100-mL glass graduated cylinder. A stopwatch was used to measure time.

- 1) t = 0 min. - Floccs are up to 1 mm, some (flocs) are spherical, others are flat.
- 2) t = 6 min. - The particles settle very rapidly. The top 5 mL is essentially clear (to the eye). Other particles are stationary and not settling at all.
- 3) t = 10 min.- The top 10 mL is essentially clear. Many of the larger particles are on the bottom of the cylinder.
- 4) t = 15 min.- Nearly all larger particles are below the 60 mL mark, though some (smaller) flocs are not settling.
- 5) t = 22 min. - The solution is not quite clear, but about 90% of the particles have settled out.

**THIS PAGE INTENTIONALLY
LEFT BLANK**

APPENDIX D
1993 HEIS DATA

91322-55
72816

1993 HEIS DATA

506172616
944321005

Table D.1. 1993 Data Available from the HEIS Database for 100 Area Wells 199-D5-15 and 199-H4-4.

	199-D5-15 ROUND: 4 B084W5 () 03/15/93 FILT: FIELD	199-D5-15 ROUND: 4 B084W5 () 03/15/93 FILT: SKINER	199-D5-15 ROUND: 4 B084W5 () 03/15/93 FILT: TMA	199-D5-15 ROUND: 4 B084W6 () 03/15/93 FILT: Y FIELD	199-D5-15 ROUND: 4 B084W6 () 03/15/93 FILT: Y SKINER
(field) conductivity	504.00. UMHO/C	504.00. UMHO/C	504.00. UMHO/C	504.00. UMHO/C	504.00. UMHO/C
(field) temperature	19.40. DEG C	19.40. DEG C	19.40. DEG C	19.40. DEG C	19.40. DEG C
Alkalinity					
Aluminum	27.00. UG/L	27.00. UG/L	27.00. UG/L	27.00. UG/L	27.00. UG/L
Antimony	18.40. UG/L	18.40. UG/L	18.40. UG/L	19.00. UG/L	19.00. UG/L
Antimony-125					
Arsenic	2.80. UG/L	2.80. UG/L	2.80. UG/L	2.00. UG/L	2.00. UG/L
Barium	88.70. UG/L	88.70. UG/L	88.70. UG/L	86.00. UG/L	86.00. UG/L
Beryllium	.50. UG/L	.50. UG/L	.50. UG/L	.90. UG/L	.90. UG/L
Bromide					
Cadmium	1.60. UG/L	1.60. UG/L	1.60. UG/L	1.40. UG/L	1.40. UG/L
Calcium	63200.00. UG/L	63200.00. UG/L	63200.00. UG/L	62200.00. UG/L	62200.00. UG/L
Cesium-137					
Chloride					
Chromium	1630.00. UG/L	1630.00. UG/L	1630.00. UG/L	1570.00. UG/L	1570.00. UG/L
Cobalt	2.50. UG/L	2.50. UG/L	2.50. UG/L	3.20. UG/L	3.20. UG/L
Cobalt-60					
Conductivity	439.00. UMHO	439.00. UMHO	439.00. UMHO		
Copper	7.50. UG/L	7.50. UG/L	7.50. UG/L	4.90. UG/L	4.90. UG/L
Cyanide					
Cyanide	UG/L	UG/L	UG/L	UG/L	UG/L
Fluoride					
Gross alpha	.58. PC1/L U	.58. PC1/L U	.58. PC1/L U		
Gross beta	8.50. PC1/L	8.50. PC1/L	8.50. PC1/L		
Iron	54.90. UG/L	54.90. UG/L	54.90. UG/L	6.00. UG/L	6.00. UG/L
Lead	2.00. UG/L W	2.00. UG/L W	2.00. UG/L W	1.20. UG/L	1.20. UG/L
Magnesium	16300.00. UG/L	16300.00. UG/L	16300.00. UG/L	16100.00. UG/L	16100.00. UG/L
Manganese	1.00. UG/L	1.00. UG/L	1.00. UG/L	1.70. UG/L	1.70. UG/L
Mercury	.13. UG/L	.13. UG/L	.13. UG/L	.10. UG/L N	.10. UG/L N
Nickel	8.50. UG/L	8.50. UG/L	8.50. UG/L	5.40. UG/L	5.40. UG/L
Nitrate					
Nitrite					
Nitrite Nitrate	12.20. mg/L	12.20. mg/L	12.20. mg/L		
Phosphate					
Potassium	4910.00. UG/L	4910.00. UG/L	4910.00. UG/L	5010.00. UG/L	5010.00. UG/L
Ruthenium-106					
Selenium	3.10. UG/L MWN	3.10. UG/L MWN	3.10. UG/L MWN	3.80. UG/L W	3.80. UG/L W
Silver	3.90. UG/L	3.90. UG/L	3.90. UG/L	4.60. UG/L	4.60. UG/L
Sodium	15800.00. UG/L	15800.00. UG/L	15800.00. UG/L	15800.00. UG/L	15800.00. UG/L
Strontium-90	1.40. PC1/L J	1.40. PC1/L J	1.40. PC1/L J		
Sulfate					
Technetium-99					
Temperature (field measurement)					
Thallium	1.90. UG/L W	1.90. UG/L W	1.90. UG/L W	1.50. UG/L	1.50. UG/L
Tin					
Total organic carbon					
Total organic halides					
Tritium	660.00. PC1/L	660.00. PC1/L	660.00. PC1/L		
Turbidity					
Uranium					
Uranium-234					
Uranium-235					
Uranium-238					
Vanadium	10.70. UG/L	10.70. UG/L	10.70. UG/L	12.20. UG/L	12.20. UG/L
Zinc	4.70. UG/L	4.70. UG/L	4.70. UG/L	2.50. UG/L	2.50. UG/L
pH Measurement	8.09. pH	8.09. pH	8.09. pH		
pH-field measurement	8.02. pH	8.02. pH	8.02. pH	8.02. pH	8.02. pH

94/3221.0507

Table D.1. (cont.)

	199-H4-4 ROUND: B07TN0 (,) 01/28/93 FILT: DATACH	199-H4-4 ROUND: B07TN0 (,) 01/28/93 FILT: FIELD	199-H4-4 ROUND: B07TN0 (,) 01/28/93 FILT: ITASRL	199-H4-4 ROUND: B07TN6 (,) 01/28/93 FILT: DATACH	199-H4-4 ROUND: B07TN6 (,) 01/28/93 FILT: ITASRL
(field) conductivity					
(field) temperature					
Alkalinity	130.00. MG/L	130.00. MG/L	130.00. MG/L		
Aluminum					
Antimony	200.00. UG/L U	200.00. UG/L U	200.00. UG/L U		
Antimony-125					
Arsenic					
Barium	40.00. UG/L	40.00. UG/L	40.00. UG/L		
Beryllium	3.00. UG/L U	3.00. UG/L U	3.00. UG/L U		
Bromide	500.00. UG/L U	500.00. UG/L U	500.00. UG/L U		
Cadmium	10.00. UG/L U	10.00. UG/L U	10.00. UG/L U		
Calcium	30000.00. UG/L	30000.00. UG/L	30000.00. UG/L		
Cesium-137					
Chloride	6700.00. UG/L	6700.00. UG/L	6700.00. UG/L		
Chromium	170.00. UG/L	170.00. UG/L	170.00. UG/L		
Cobalt	20.00. UG/L U	20.00. UG/L U	20.00. UG/L U		
Cobalt-60					
Conductivity	533.00.	533.00.	533.00.		
Copper	20.00. UG/L U	20.00. UG/L U	20.00. UG/L U		
Cyanide				20.00. UG/L U	20.00. UG/L U
Cyanide					
Fluoride	300.00. UG/L	300.00. UG/L	300.00. UG/L		
Gross alpha	43.40. PC1/L	43.40. PC1/L	43.40. PC1/L		
Gross beta	100.00. PC1/L	100.00. PC1/L	100.00. PC1/L		
Iron	18000.00. UG/L	18000.00. UG/L	18000.00. UG/L		
Lead					
Magnesium	5000.00. UG/L	5000.00. UG/L	5000.00. UG/L		
Manganese	30.00. UG/L	30.00. UG/L	30.00. UG/L		
Mercury					
Nickel	40.00. UG/L	40.00. UG/L	40.00. UG/L		
Nitrate	87000.00. UG/L	87000.00. UG/L	87000.00. UG/L		
Nitrite	200.00. UG/L U	200.00. UG/L U	200.00. UG/L U		
Nitrite Nitrate					
Phosphate	400.00. UG/L U	400.00. UG/L U	400.00. UG/L U		
Potassium	4600.00. UG/L	4600.00. UG/L	4600.00. UG/L		
Ruthenium-106					
Selenium					
Silver	20.00. UG/L U	20.00. UG/L U	20.00. UG/L U		
Sodium	75000.00. UG/L	75000.00. UG/L	75000.00. UG/L		
Strontium-90				.97. PC1/L U	.97. PC1/L U
Sulfate	44000.00. UG/L	44000.00. UG/L	44000.00. UG/L		
Technetium-99	319.00. PC1/L	319.00. PC1/L	319.00. PC1/L		
Temperature (field measurement)	18.20.	18.20.	18.20.		
Thallium					
Tin	100.00. UG/L U	100.00. UG/L U	100.00. UG/L U		
Total organic carbon	1000.00. UG/L U	1000.00. UG/L U	1000.00. UG/L U		
Total organic halides	10.00. UG/L	10.00. UG/L	10.00. UG/L		
Tritium				1730.00. PC1/L	1730.00. PC1/L
Turbidity	.30. NTU	.30. NTU	.30. NTU		
Uranium	32.30. UG/L	32.30. UG/L	32.30. UG/L		
Uranium-234					
Uranium-235					
Uranium-238					
Vanadium	30.00. UG/L U	30.00. UG/L U	30.00. UG/L U		
Zinc	20.00. UG/L	20.00. UG/L	20.00. UG/L		
pH Measurement	7.45.	7.45.	7.45.		
pH-field measurement					

94/3221.0508

Table D.1. (cont.)

	199-H4-4 B08531 (,) 02/24/93 FILT: DATACH	ROUND: FIELD	199-H4-4 B08531 (,) 02/24/93 FILT: FIELD	ROUND: FIELD	199-H4-4 B08531 (,) 02/24/93 FILT: ITASRL	ROUND: FIELD	199-H4-4 B086N5 (,) 03/10/93 FILT: ITASRL	ROUND: FIELD
field conductivity								
field temperature								
Alkalinity								
Aluminum								
Antimony	200.00	UG/L U	200.00	UG/L U	200.00	UG/L U		
Antimony-125						2.10	PCI/L	2.10
Arsenic								
Barium	20.00	UG/L	20.00	UG/L	20.00	UG/L		
Beryllium	3.00	UG/L U	3.00	UG/L U	3.00	UG/L U		
Bromide	500.00	UG/L U	500.00	UG/L U	500.00	UG/L U		
Cadmium	10.00	UG/L U	10.00	UG/L U	10.00	UG/L U		
Calcium	19000.00	UG/L	19000.00	UG/L	19000.00	UG/L		
Cesium-137						6.94	PCI/L	6.94
Chloride	5900.00	UG/L	5900.00	UG/L	5900.00	UG/L		
Chromium	100.00	UG/L	100.00	UG/L	100.00	UG/L		
Cobalt	20.00	UG/L U	20.00	UG/L U	20.00	UG/L U		
Cobalt-60						4.37	PCI/L	4.37
Conductivity	546.00		546.00		546.00		538.00	UMHO
Copper	20.00	UG/L U	20.00	UG/L U	20.00	UG/L U		
Cyanide								
Cyanide								
Fluoride	600.00	UG/L	600.00	UG/L	600.00	UG/L		
Gross alpha	32.50	PCI/L	32.50	PCI/L	32.50	PCI/L	37.70	PCI/L
Gross beta	58.80	PCI/L	58.80	PCI/L	58.80	PCI/L	89.80	PCI/L
Iron	280.00	UG/L	280.00	UG/L	280.00	UG/L		
Lead								
Magnesium	1100.00	UG/L	1100.00	UG/L	1100.00	UG/L		
Manganese	10.00	UG/L U	10.00	UG/L U	10.00	UG/L U		
Mercury								
Nickel	30.00	UG/L U	30.00	UG/L U	30.00	UG/L U		
Nitrate	58000.00	UG/L	58000.00	UG/L	58000.00	UG/L		
Nitrite	200.00	UG/L U	200.00	UG/L U	200.00	UG/L U		
Nitrite Nitrate								
Phosphate	400.00	UG/L U	400.00	UG/L U	400.00	UG/L U		
Potassium	4300.00	UG/L	4300.00	UG/L	4300.00	UG/L		
Ruthenium-106						49.30	PCI/L	49.30
Selenium								
Silver	20.00	UG/L U	20.00	UG/L U	20.00	UG/L U		
Sodium	75000.00	UG/L	75000.00	UG/L	75000.00	UG/L		
Strontium-90								
Sulfate	39000.00	UG/L	39000.00	UG/L	39000.00	UG/L		
Technetium-99								
Temperature (field measurement)	17.70		17.70		17.70		18.50	DEG-C
Thallium								
Tin	100.00	UG/L U	100.00	UG/L U	100.00	UG/L U		
Total organic carbon								
Total organic halides								
Tritium						1570.00	PCI/L	1570.00
Turbidity								
Uranium						36.50	UG/L	36.50
Uranium-234						23.10	PCI/L	23.10
Uranium-235						.96	PCI/L	.96
Uranium-238						16.80	PCI/L	16.80
Vanadium	30.00	UG/L U	30.00	UG/L U	30.00	UG/L U		
Zinc	10.00	UG/L	10.00	UG/L	10.00	UG/L		
pH Measurement	7.34		7.34		7.34		8.15	PH
pH-field measurement								

9413221.0509

Table D.1. (cont.)

	199-H4-4 B08970 (,) 03/10/93 FILT: DATACH	ROUND: FIELD	199-H4-4 B08970 (,) 03/10/93 FILT: FIELD	ROUND: FIELD	199-H4-4 B08970 (,) 03/10/93 FILT: ITASRL	ROUND: FIELD	199-H4-4 B08CP1 (,) 04/01/93 FILT: DATACH	ROUND: FIELD	199-H4-4 B08CP1 (,) 04/01/93 FILT: FIELD	ROUND: FIELD
(field) conductivity										
(field) temperature										
Alkalinity							140.00. MG/L		140.00. MG/L	
Aluminum										
Antimony	200.00. UG/L	U	200.00. UG/L	U	200.00. UG/L	U	200.00. UG/L	U	200.00. UG/L	U
Antimony-125										
Arsenic										
Barium	30.00. UG/L		30.00. UG/L		30.00. UG/L		30.00. UG/L		30.00. UG/L	
Beryllium	3.00. UG/L	U	3.00. UG/L	U	3.00. UG/L	U	3.00. UG/L	U	3.00. UG/L	U
Bromide	500.00. UG/L	U	500.00. UG/L	U	500.00. UG/L	U	500.00. UG/L	U	500.00. UG/L	U
Cadmium	10.00. UG/L	U	10.00. UG/L	U	10.00. UG/L	U	10.00. UG/L	U	10.00. UG/L	U
Calcium	23000.00. UG/L		23000.00. UG/L		23000.00. UG/L		23000.00. UG/L		23000.00. UG/L	
Cesium-137										
Chloride	6900.00. UG/L		6900.00. UG/L		6900.00. UG/L		7100.00. UG/L		7100.00. UG/L	
Chromium	110.00. UG/L		110.00. UG/L		110.00. UG/L		130.00. UG/L		130.00. UG/L	
Cobalt	20.00. UG/L	U	20.00. UG/L	U	20.00. UG/L	U	20.00. UG/L	U	20.00. UG/L	U
Cobalt-60										
Conductivity	538.00.		538.00.		538.00.		551.00.		551.00.	
Copper	20.00. UG/L	U	20.00. UG/L	U	20.00. UG/L	U	20.00. UG/L	U	20.00. UG/L	U
Cyanide										
Cyanide										
Fluoride	600.00. UG/L		600.00. UG/L		600.00. UG/L		600.00. UG/L		600.00. UG/L	
Gross alpha	37.60. PC1/L		37.60. PC1/L		37.60. PC1/L		47.10. PC1/L		47.10. PC1/L	
Gross beta	95.50. PC1/L		95.50. PC1/L		95.50. PC1/L		94.60. PC1/L		94.60. PC1/L	
Iron	51.00. UG/L		51.00. UG/L		51.00. UG/L		1500.00. UG/L		1500.00. UG/L	
Lead										
Magnesium	3800.00. UG/L		3800.00. UG/L		3800.00. UG/L		3600.00. UG/L		3600.00. UG/L	
Manganese	10.00. UG/L	U	10.00. UG/L	U	10.00. UG/L	U	20.00. UG/L		20.00. UG/L	
Mercury										
Nickel	30.00. UG/L	U	30.00. UG/L	U	30.00. UG/L	U	30.00. UG/L	U	30.00. UG/L	U
Nitrate	88000.00. UG/L		88000.00. UG/L		88000.00. UG/L		93000.00. UG/L		93000.00. UG/L	
Nitrate	200.00. UG/L	U	200.00. UG/L	U	200.00. UG/L	U	200.00. UG/L	U	200.00. UG/L	U
Nitrate-Nitrate										
Phosphate	400.00. UG/L	U	400.00. UG/L	U	400.00. UG/L	U	400.00. UG/L	U	400.00. UG/L	U
Potassium	4500.00. UG/L		4500.00. UG/L		4500.00. UG/L		3900.00. UG/L		3900.00. UG/L	
Ruthenium-106										
Selenium										
Silver	20.00. UG/L	U	20.00. UG/L	U	20.00. UG/L	U	20.00. UG/L	U	20.00. UG/L	U
Sodium	84000.00. UG/L		84000.00. UG/L		84000.00. UG/L		88000.00. UG/L		88000.00. UG/L	
Strontium-90										
Sulfate	43000.00. UG/L		43000.00. UG/L		43000.00. UG/L		48000.00. UG/L		48000.00. UG/L	
Technetium-99							340.00. PC1/L		340.00. PC1/L	
Temperature (field measurement)	18.50.		18.50.		18.50.		18.70.		18.70.	
Thallium										
Tin	100.00. UG/L	U	100.00. UG/L	U	100.00. UG/L	U	100.00. UG/L	U	100.00. UG/L	U
Total organic carbon							1000.00. UG/L	U	1000.00. UG/L	U
Total organic halides							30.00. UG/L	B	30.00. UG/L	B
Tritium										
Turbidity							6.00. NTU		6.00. NTU	
Uranium							534.00. UG/L		534.00. UG/L	
Uranium-234										
Uranium-235										
Uranium-238										
Vanadium	30.00. UG/L	U	30.00. UG/L	U	30.00. UG/L	U	30.00. UG/L	U	30.00. UG/L	U
Zinc	10.00. UG/L	U	10.00. UG/L	U	10.00. UG/L	U	20.00. UG/L		20.00. UG/L	
pH Measurement	8.15.		8.15.		8.15.		7.83.		7.83.	
pH-field measurement										

94/3221.0510

Table D.1. (cont.)

	199-H4-4 B08CPI (,) 04/01/93 FILT: ITASRL	ROUND:	199-H4-4 B08JC1 (,) 05/07/93 FILT: DATAH	ROUND:	199-H4-4 B08JC1 (,) 05/07/93 FILT: FIELD	ROUND:	199-H4-4 B08JC1 (,) 05/07/93 FILT: ITASRL	ROUND:	199-H4-4 B08MG4 (,) 06/08/93 FILT: FIELD	ROUND:
(field) conductivity										
(field) temperature										
Alkalinity	140.00.	MG/L								
Aluminum	200.00.	UG/L	U	49.00.	UG/L	L	49.00.	UG/L	L	
Antimony				200.00.	UG/L	U	200.00.	UG/L	U	
Antimony-125										11.60. PCI/L
Arsenic	30.00.	UG/L		30.00.	UG/L		30.00.	UG/L		
Barium	3.00.	UG/L	U	3.00.	UG/L	U	3.00.	UG/L	U	
Beryllium	500.00.	UG/L	U	500.00.	UG/L	U	500.00.	UG/L	U	
Bromide	10.00.	UG/L	U	10.00.	UG/L	U	10.00.	UG/L	U	
Cadmium	23000.00.	UG/L		23000.00.	UG/L		22000.00.	UG/L		
Calcium										5.55. PCI/L
Cesium-137	7100.00.	UG/L		6400.00.	UG/L		6400.00.	UG/L		
Chloride	100.00.	UG/L		100.00.	UG/L		100.00.	UG/L		
Chromium	20.00.	UG/L	U	20.00.	UG/L	U	20.00.	UG/L	U	
Cobalt										6.15. PCI/L
Cobalt-60										***** DMHG/C
Conductivity	561.00.			560.00.			560.00.			
Copper	20.00.	UG/L	U	20.00.	UG/L	U	20.00.	UG/L	U	
Cyanide										
Cyanide										
Fluoride	500.00.	UG/L		400.00.	UG/L	EC	400.00.	UG/L	EC	
Gross alpha	47.10.	PCI/L		27.90.	PCI/L		27.90.	PCI/L		7.41. PCI/L
Gross beta	94.60.	PCI/L		97.90.	PCI/L		97.90.	PCI/L		13.70. PCI/L
Iron	1500.00.	UG/L		250.00.	UG/L		250.00.	UG/L		
Lead										
Magnesium	3500.00.	UG/L		3500.00.	UG/L		3500.00.	UG/L		
Manganese	3.20.	UG/L	L	3.20.	UG/L	L	3.20.	UG/L	L	
Mercury										
Nickel	30.00.	UG/L	U	30.00.	UG/L	U	30.00.	UG/L	U	
Nitrate	85000.00.	UG/L		85000.00.	UG/L		85000.00.	UG/L		
Nitrite	200.00.	UG/L	U	200.00.	UG/L	U	200.00.	UG/L	U	
Nitrite Nitrate										
Phosphate	400.00.	UG/L	U	400.00.	UG/L	U	400.00.	UG/L	U	
Potassium	3900.00.	UG/L		4000.00.	UG/L		4000.00.	UG/L		
Ruthenium-101										17.80. PCI/L
Selenium										
Silver	20.00.	UG/L	U	20.00.	UG/L	U	20.00.	UG/L	U	
Sodium	88000.00.	UG/L		81000.00.	UG/L		81000.00.	UG/L		
Strontium-90										
Sulfate	43000.00.	UG/L		43000.00.	UG/L		43000.00.	UG/L		
Technetium-99	340.00.	PCI/L								
Temperature (field measurement)	18.70.			18.90.			18.90.			***** DEG C
Thallium										
Tin	100.00.	UG/L	U		UG/L	U		UG/L	U	
Total organic carbon	1000.00.	UG/L	U							
Total organic halides	30.00.	UG/L	B							
Tritium										562.00. PCI/L
Turbidity	6.00.	NTU								
Uranium	534.00.	UG/L								3.37. UG/L
Uranium-234										
Uranium-235										
Uranium-238										
Vanadium	30.00.	UG/L	U	5.20.	UG/L	L	5.20.	UG/L	L	
Zinc	20.00.	UG/L		10.00.	UG/L		10.00.	UG/L		
pH Measurement	7.83.			7.92.			7.92.			7.82. PH
pH-field measurement										

94/3221-0511

Table D.1. (cont.)

	199-H4-4 ROUND: B08MG4 (,) 06/08/93 FILT: ITASRL	199-H4-4 ROUND: B08LS0 (,) 06/14/93 FILT: DATACH	199-H4-4 ROUND: B08LS0 (,) 06/14/93 FILT: FIELD	199-H4-4 ROUND: B08LS0 (,) 06/14/93 FILT: ITASRL	199-H4-4 ROUND: B08QZ0 (,) 07/13/93 FILT: DATACH
(field) conductivity					
(field) temperature					
Alkalinity		49.00. UG/L L	49.00. UG/L L	49.00. UG/L L	100.00. MG/L
Aluminum		208.00. UG/L U	200.00. UG/L U	200.00. UG/L U	32.50. UG/L U
Antimony					69.40. UG/L U
Antimony-125	11.60. PCI/L				
Arsenic		23.00. UG/L	23.00. UG/L	23.00. UG/L	21.00. UG/L
Barium		3.00. UG/L U	3.00. UG/L U	3.00. UG/L U	.81. UG/L U
Beryllium		500.00. UG/L U	500.00. UG/L U	500.00. UG/L U	52.80. UG/L U
Bromide		10.00. UG/L U	10.00. UG/L U	10.00. UG/L U	4.70. UG/L U
Cadmium		24000.00. UG/L	24000.00. UG/L	24000.00. UG/L	21000.00. UG/L
Calcium					
Cesium-137	5.55. PCI/L	2900.00. UG/L	2900.00. UG/L	2900.00. UG/L	4000.00. UG/L
Chloride		48.00. UG/L	48.00. UG/L	48.00. UG/L	75.00. UG/L
Chromium		20.00. UG/L U	20.00. UG/L U	20.00. UG/L U	4.05. UG/L U
Cobalt					
Cobalt-60	6.15. PCI/L				
Conductivity	***** UMHO/C	260.00.	260.00.	260.00.	355.00.
Copper		20.00. UG/L U	20.00. UG/L U	20.00. UG/L U	2.65. UG/L U
Cyanide					
Cyanide					
Fluoride		300.00. UG/L	300.00. UG/L	300.00. UG/L	500.00. UG/L
Gross alpha	7.41. PCI/L	8.57. PCI/L	8.57. PCI/L	8.57. PCI/L	14.20. PCI/L
Gross beta	13.70. PCI/L	17.40. PCI/L	17.40. PCI/L	17.40. PCI/L	36.50. PCI/L
Iron		210.00. UG/L	210.00. UG/L	210.00. UG/L	250.00. UG/L
Lead					
Magnesium		4300.00. UG/L	4300.00. UG/L	4300.00. UG/L	3700.00. UG/L
Manganese		2.50. UG/L L	2.50. UG/L L	2.50. UG/L L	4.70. UG/L L
Mercury					
Nickel		10.00. UG/L U	10.00. UG/L U	10.00. UG/L U	17.90. UG/L U
Nitrate		20000.00. UG/L	20000.00. UG/L	20000.00. UG/L	36000.00. UG/L
Nitrite		200.00. UG/L U	200.00. UG/L U	200.00. UG/L U	38.30. UG/L U
Nitrite Nitrate					
Phosphate		400.00. UG/L U	400.00. UG/L U	400.00. UG/L U	147.00. UG/L U
Potassium		3200.00. UG/L	3200.00. UG/L	3200.00. UG/L	3000.00. UG/L
Ruthenium-106	17.80. PCI/L				
Selenium					
Silver		20.00. UG/L U	20.00. UG/L U	20.00. UG/L U	2.87. UG/L U
Sodium		24000.00. UG/L	24000.00. UG/L	24000.00. UG/L	36000.00. UG/L
Strontium 90					
Sulfate		21000.00. UG/L	21000.00. UG/L	21000.00. UG/L	32000.00. UG/L
Technetium 99					
Temperature (field measurement)	***** DEG C	17.70.	17.70.	17.70.	114.00. PCI/L
Thallium					18.20.
Tin		UG/L U	UG/L U	UG/L U	51.10. UG/L U
Total organic carbon					700.00. UG/L L
Total organic halides					8.00. UG/L U
Tritium	562.00. PCI/L				
Turbidity					4.80. NTU
Uranium	3.37. UG/L				16.20. UG/L
Uranium-234					
Uranium-235					
Uranium-238					
Vanadium		7.10. UG/L L	7.10. UG/L L	7.10. UG/L L	22.00. UG/L L
Zinc		10.00. UG/L U	10.00. UG/L U	10.00. UG/L U	9.60. UG/L L
pH Measurement	7.82. PH	7.90.	7.90.	7.90.	8.08.
pH-field measurement					

94/3221.0512

Table D.1. (cont.)

	199-H4-4 B08QZ0 () 07/13/93 FILT: FIELD	ROUND:	199-H4-4 B08QZ0 () 07/13/93 FILT: ITASRL	ROUND:	199-H4-4 B08Z16 () 08/18/93 FILT: ITASRL	ROUND:	199-H4-4 B090T4 () 08/18/93 FILT: DATACH	ROUND:	199-H4-4 B090T4 () 08/18/93 FILT: FIELD	ROUND:
(field) conductivity										
(field) temperature										
Alkalinity	100.00.	MG/L	100.00.	MG/L			32.50.	UG/L	32.50.	UG/L
Aluminum	32.50.	UG/L	32.50.	UG/L			69.40.	UG/L	69.40.	UG/L
Antimony	69.40.	UG/L	69.40.	UG/L						
Antimony-125					11.10.	PCI/L				
Arsenic	21.00.	UG/L	21.00.	UG/L			30.00.	UG/L	30.00.	UG/L
Barium	.81.	UG/L	.81.	UG/L			.81.	UG/L	.81.	UG/L
Beryllium	52.80.	UG/L	52.80.	UG/L						
Bromine	4.70.	UG/L	4.70.	UG/L			4.70.	UG/L	4.70.	UG/L
Cadmium	21000.00.	UG/L	21000.00.	UG/L			25000.00.	UG/L	25000.00.	UG/L
Calcium					2.61.	PCI/L				
Cesium-137	4000.00.	UG/L	4000.00.	UG/L			100.00.	UG/L	100.00.	UG/L
Chloride	75.00.	UG/L	75.00.	UG/L			6.00.	UG/L	6.00.	UG/L
Chromium	4.05.	UG/L	4.05.	UG/L						
Cobalt					5.59.	PCI/L				
Cobalt-60	555.00.		555.00.				581.00.		581.00.	
Conductivity	2.65.	UG/L	2.65.	UG/L			2.65.	UG/L	2.65.	UG/L
Copper										
Cyanide										
Cyanide	500.00.	UG/L	500.00.	UG/L						
Fluoride	14.20.	PCI/L	14.20.	PCI/L						
Gross alpha	36.50.	PCI/L	36.50.	PCI/L						
Gross beta	250.00.	UG/L	250.00.	UG/L			290.00.	UG/L	290.00.	UG/L
Iron										
Lead	3700.00.	UG/L	3700.00.	UG/L			4200.00.	UG/L	4200.00.	UG/L
Magnesium	4.70.	UG/L	4.70.	UG/L			4.80.	UG/L	4.80.	UG/L
Manganese										
Mercury	17.90.	UG/L	17.90.	UG/L			17.90.	UG/L	17.90.	UG/L
Molybdenum	36000.00.	UG/L	36000.00.	UG/L						
Nitrate	38.30.	UG/L	38.30.	UG/L						
Nitrite										
Nitrite Nitrate	147.00.	UG/L	147.00.	UG/L			3400.00.	UG/L	3400.00.	UG/L
Phosphate	3000.00.	UG/L	3000.00.	UG/L						
Potassium					3.63.	PCI/L				
Ruthenium-106										
Selenium	2.87.	UG/L	2.87.	UG/L			3.40.	UG/L	3.40.	UG/L
Silver	36000.00.	UG/L	36000.00.	UG/L			76000.00.	UG/L	76000.00.	UG/L
Sodium										
Strontium-90										
Sulfate	32000.00.	UG/L	32000.00.	UG/L						
Temperature 99	114.00.	°F/L	114.00.	°F/L			18.60.		18.60.	
Temperature (field measurement)	18.20.		18.20.							
Thallium							51.10.	UG/L	51.10.	UG/L
Tin	51.10.	UG/L	51.10.	UG/L						
Total organic carbon	700.00.	UG/L	700.00.	UG/L						
Total organic halides	8.00.	UG/L	8.00.	UG/L						
Titanium										
Turbidity	4.80.	NTU	4.80.	NTU						
Uranium	16.20.	UG/L	16.20.	UG/L	14.00.	UG/L				
Uranium-234										
Uranium-235										
Uranium-238										
Vanadium	22.00.	UG/L	22.00.	UG/L			8.00.	UG/L	8.00.	UG/L
Zinc	9.60.	UG/L	9.60.	UG/L			9.10.	UG/L	9.10.	UG/L
pH Measurement	8.08.		8.08.				8.00.		8.00.	
pH-field measurement										

94/3221-0513

Table D.1. (cont.)

	199-H4-4 ROUND: B09639 (,) 09/07/93 FILT: DATACH	199-H4-4 ROUND: B09639 (,) 09/07/93 FILT: FIELD	199-H4-4 ROUND: B09639 (,) 09/07/93 FILT: ITASRL	199-H4-4 ROUND: B099T0 (,) 10/06/93 FILT: FIELD	199-H4-4 ROUND: B099T0 (,) 10/06/93 FILT: ITASRL
(field) conductivity					
(field) temperature					
Alkalinity					
Aluminum					
Antimony					
Antimony-125					
Arsenic					
Barium					
Beryllium					
Bromide	52.80. UG/L U	52.80. UG/L U	52.80. UG/L U		
Cadmium					
Calcium					
Cesium-137					
Chloride	5800.00. UG/L	5800.00. UG/L	5800.00. UG/L		
Chromium					
Cobalt					
Cobalt-60					
Conductivity	596.00.	596.00.	596.00.	760.00.	760.00.
Copper					
Cyanide					
Fluoride	400.00. UG/L	400.00. UG/L	400.00. UG/L		
Gross alpha	39.40. PC1/L	39.40. PC1/L	39.40. PC1/L	31.10. PC1/L	31.10. PC1/L
Gross beta	130.00. PC1/L	130.00. PC1/L	130.00. PC1/L	199.00. PC1/L	199.00. PC1/L
Iron					
Lead					
Magnesium					
Manganese					
Mercury					
Nickel	110000.00. UG/L D	110000.00. UG/L D	110000.00. UG/L D		
Nitrate	38.30. UG/L U	38.30. UG/L U	38.30. UG/L U		
Nitrite					
Nitrite Nitrate	147.00. UG/L U	147.00. UG/L U	147.00. UG/L U		
Phosphate					
Potassium					
Ruthenium-106					
Selenium					
Silver					
Sodium					
Strontium-90					
Sulfate	57000.00. UG/L D	57000.00. UG/L D	57000.00. UG/L D		
Technetium-99					
Temperature (field measurement)	18.20.	18.20.	18.20.	18.60.	18.60.
Thallium					
Tin					
Total organic carbon					
Total organic halides					
Tritium					
Turbidity					
Uranium					
Uranium-234					
Uranium-235					
Uranium-238					
Vanadium					
Zinc	7.91.	7.91.	7.91.	7.94.	7.94.
pH Measurement					
pH field measurement					